No .....
PROPERTY OF
A. E. STALEY MFG. CO
DECATUR ILLINOIS
LABORATORY LIBRARY

UNIVERSITY OF
ILLINOIS LIBRARY
AT URBANA-CHAMPAIGN

Digitized by the Internet Archive
in 2018 with funding from
University of Illinois Urbana-Champaign Alternates

https://archive.org/details/journalofchemica62chem

JOURNAL

OF

THE CHEMICAL SOCIETY.

Committee of Publication:

H. E. Armstrong, Ph.D., F.R.S.
E. Atkinson, Ph.D.
A. Crum Brown, D.Sc., F.R.S.
Wyndham R. Dunstan.
R. Meldola, F.R.S.
H. F. Morley, M.A., D.Sc.
Hugo Müller, Ph.D., F.R.S.
W. H. Perkin, Ph.D., F.R.S.
J. Millar Thomson, F.R.S.E.
T. E. Thorpe, Ph.D., F.R.S.
W. P. Wynne, B.Sc.

Editor:
C. E. Groves, F.R.S.

Sub-Editor:
A. J. Greenaway.

Abstractors:

S. B. Asher Aron.
C. F. Baker, Ph.D., B.Sc.
D. Bendix.
A. G. Bloxam.
C. H. Bothamley.
B. H. Brough.
H. G. Colman, Ph.D.
H. Crompton.
L. De Koningh.
W. D. Halliburton, M.D., B.Sc., F.R.S.
F. S. Kipping, Ph.D., D.Sc.
J. W. Leather, Ph.D.
A. R. Ling.
D. A. Louis.
N. H. J. Miller, Ph.D.
G. T. Moody, D.Sc.
J. M. H. Munro, D.Sc.
T. G. Nicholson.
W. J. Pope.
E. W. Prevost, Ph.D.
E. C. Rossiter.
R. Routledge, B.Sc.
M. J. Salter.
W. Tate.
James Taylor, B.Sc.
L. T. Thorne, Ph.D.
J. B. Tingle, Ph.D.
J. Wade, B.Sc. (Jn. W.)
J. Walker, D.Sc., Ph.D. (J. W.)

Vol. LXII. Part I.

1892. ABSTRACTS.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1892.

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,
ST. MARTIN'S LANE.

540.5
J0C
V.162
cop.2

UNIVERSITY OF ILLINOIS
AGRICULTURE LIBRARY

AGX

CONTENTS.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

General and Physical Chemistry.

PAGE

DUSSAUD (L.). Refraction and Dispersion of Sodium Chlorate . . . 1
AYMONNET. Relation between the Index of Refraction, Density, Molecular Weight, and Diathermanous Power of a Substance. 1
HAITINGER (L.). Emission Spectra of Neodymium and Præseodymium Oxides and of Luminous Solids containing Neodymium 2
BERTHELOT (D.). Study of the Chemical Neutralisation of Acids and Bases, by means of their Electrical Conductivities 2
HINRICHS (G.). Calculation of the Specific Heat of Liquids . . . 2
LE CHATELIER (H.). Second Law of Thermodynamics and its Application to Chemical Phenomena 3
AMAGAT (E. H.). New Isothermal Curves for Carbonic Anhydride . . 3
PIGEON (L.). Heat of Formation of Platinic Bromide and its Principal Compounds 3
BERTHELOT and MATIGNON. Heats of Combustion and Formation of Nitrobenzenes 4
STOHMANN (F.) and H. LANGBEIN. Calorific Value of Food Constituents and their Derivatives 4
VERNON (H. M.). Maximum Density of Water 7
SCHEEL (C.). Expansion of Water 7
LEDUC (A.). Dilatation of Phosphorus and its Change of Volume at the Melting Point 7
TRAUBE (J.). Capillary Constants of Salts at their Melting Points . . 7
NICOL (W. W. J.). Mutual Solubility of Salts in Water 8
TRAUBE (J.). Cryoscopic Behaviour of Dilute Solutions 8
VERNEUIL (A.). Automatic Return of Mercury in Sprengel Pumps . . 8
GAWALOVSKI (A.). Block Support for Tubes 9
BEHRENS (H.). Formation of Mixed Crystals 10
VANNI (J.). Apparent Variability of the Electrical Equivalent of Copper . 105
PAGLIANI (S.). New Method of Measuring Electromotive Forces and Electrical Resistance 105
MATIGNON (C.). Characteristic Difference between Alcohol Radicles united directly with Carbon or with Nitrogen 106
MAREK (W.). Expansion of Water 106
VERNON (H. M.). Molecular Weights of Liquids as evinced by their Boiling Points 107
BOHR (C.) and J. BOCK. Solubility of Gases in Water 107
WANKLYN (J. A.) and W. JOHNSTONE. Nature of Solution. . . . 107
PICKERING (S. U.). Strong Solutions and the Dissociation Hypothesis . 108
PICKERING (S. U.). Cryoscopy of Cane-sugar Solutions 109
BERTHELOT (D.). Existence of Acid or Basic Salts of Monobasic Acids in very dilute Solution 110
MAGNANINI (G.). Catalytic Influence of Acids on the Velocity of the Reaction between Hydrogen Peroxide and Hydriodic Acid 110
STOKES (G. G.). Optical Proof of the Existence of Suspended Matter in Flames 111

PAGE

Richardson (A.). Measurement of Light Intensity by the Expansion of Chlorine. 253
Nasini (R.). Application of Ketteler's Formulæ to Optical Chemistry . 253
Vignon (L.). Rotatory Power of Silk. 254
Gore (G.). Changes of Voltaic Energy of Alloys during Fusion. . . 254
Speyers (C. L.). Electromotive Forces of Metallic Salts 255
Magnanini (G.). Influence of Boric Acid on the Electrical Conductivity of Aqueous Solutions of Organic Acids 256
Swinburne (J.). Some Points on Electrolysis 257
Gore (G.). Relation of E.M.F. to Latent Heat, Specific Gravity, &c., of Electrolytes 257
Obach (B.). Specific Inductive Capacity and Latent Heat of Vaporisation. 258
Blümcke (A.). Change of the Empirical and Theoretical Isothermals of Mixtures of two Substances with the Temperature. 259
Cattaneo (C.). Thermal Expansion of Liquid Bismuth 259
Hinrichs (G.). Calculation of the Boiling Points of Normal Isomeric Ethereal Salts of the Fatty Series 260
Mahler (P.). Calorimetry. 260
Massol (G.). Thermal Constants of Active Malic Acid and Potassium and Sodium Malates 260
Berthelot and Matignon. Heat of Formation of Hydrazine: Hydrazoic Acid 261
Van Deventer (C. M.) and L. T. Reicher. Formation of Salts in Alcoholic Solution 262
Schmidt (G. C.). Critical Temperatures of Mixed Liquids. . . . 262
Charpy (G.). Vapour Pressure of Aqueous Solutions of Cobalt Chloride . 263
Del Lungo (C.). Pressure and Specific Volume of Saturated Vapours . 263
Magnanini (G.). Freezing Points of Aqueous Solutions of Boric Acid and Mannitol 263
Walker (J.). The New Theories of Solution 264
Wanklyn (J. A.), W. Johnstone, and W. J. Cooper. Change of Volume on Dissolution 264
Trevor (J. E.). Mutual Solubility of Salts in Water. 264
Roozeboom (H. W. B.). Solubility of Mixed Crystals, especially of two Isomorphous Substances. 265
Roozeboom (H. W. B.). Solubility of Mixed Crystals of Potassium and Thallium Chlorates 266
Walden (P.). Affinity Coefficients of Organic Acids and their Relation to Chemical Constitution 266
Ostwald (W.). Chemical Action at a Distance 268
Pickering (S. U.). Chemical Action at a Distance 269
Lehmann (O.). Artificial Colouring of Crystals 269
Collot (A.). Rapid Weighing on Precision Balances. 270
Essner (J. C.). Siphon for Hot Liquids, &c. 270
Markovsky (G.). E.M.F. of Gas Batteries 393
Pellat (H.). Electrical Behaviour of Metals in Salt Solutions . . . 393
Braun (F.). Electrostenolysis 393
Braun (F.). Electrocapillary Reactions 394
Warren (H. N.). Electrolytic Preparation of Metallic Alloys . . . 394
Berthelot (D.). Basicity of Phosphoric Acid 394
Planck (M.). Recent Developments of the Mechanical Theory of Heat . 395
Massol (G.). Thermochemistry of Bibasic Organic Acids 395
Mahler (P.). Distillation of Coal 395
Küster (F. W.). Freezing Point of Isomorphous Mixtures . . . 396
Hinrichs (G.). Pressure of Saturated Water Vapour 396
Schmidt (G. C.). Vapour Tension of Homologous Compounds . . . 396
Coleman (J. B.). Rapid Method of Solution in the Cold 397
Setschenow (J.). Analogies between Solutions of a Gas and of a Salt . 397
Étard (A.). State of Salts in Solution: Sodium Sulphate and Strontium Chloride 397

PAGE

Boisbaudran (L. de). Supersaturation 393
Wildermann (M.) and S. Aisinmann. Velocity of the Reaction between Alcoholic Potash and Alkyl Halides 399
Guye (P. A.). Molecular Dissymmetry 399
Lunge (G.). Levelling Instrument for Gasometric Work 400
Evers (F.). New Condenser for Laboratory Purposes 400
Newth (G. S.). Lecture Experiment: Dissociation of Phosphonium Bromide 401
Gouy. Electrocapillary Phenomena and Differences of Contact Potential . 553
Schall (C.). Determination of Vapour Densities under Diminished Pressure 553
Juillard and Curchod. Depression of the Melting Point 556
Winkler (L. W.). Absorption of Gases by Liquids 556
Tammann (G.). Measurement of Osmotic Pressure 556
Natanson (L.). Law of Thermodynamical Coincidence and its Application to the Theory of Solution 557
Étard (A.). Organic Liquids as Solvents for Metallic Salts 558
Van Deventer (C. M.) and H. J. Van de Stadt. Theory of the Solubility Curve 559
Pickering (S. U.). Theory of Residual Chemical Affinity as an Explanation for the Physical Nature of Solutions 559
Schreinemakers (F. A. H.). Equilibrium of Double Salts of Lead and Potassium Iodides with their Aqueous Solution 560
Nernst (W.). Solubility of Mixed Crystals 560
Tammann (G.) and W. Nernst. Maximum Tension with which Hydrogen is set free from Solution by Metals 561
Schütze (M.). Colour and Constitution of Compounds 561
Bassett (H.). Tabular Expression of the Periodic Relations of the Elements 562
Biltz (H.). Lecture Experiment on the Diffusion of Gases 562
Meyer (V.). Lecture Experiments on Oxy-hydrogen Gas 562
Wilm (T.). Lecture Experiment 563
Quincke (G.). Relations between Compressibility and Indices of Refraction of Liquids 669
Le Bel (J. A.). Rotatory Power of Diacetyltartaric Derivatives . . 669
Colson (A.). Stereochemistry of Diacetyltartaric Acid 669
Negbaur (W.). Practical Form of the Latimer-Clark Standard Cell . . 669
Negbaur (W.). Standard Cell for Small Differences of Potential . . 670
Negbaur (W.). Potential Differences at the Surfaces of Contact of very Dilute Solutions 671
Nernst (W.). Potential Difference of Dilute Solutions 671
Nernst (W.) and R. Pauli. Electromotive Activity of the Ions . . 671
Shields (J.). Conductivity of Lead Dioxide 672
Bachmetéeff (P.). Magnetism and Atomic Weight 672
Henrichsen (S.). Magnetism of Organic Compounds 672
Richards (J. W.). Specific Heat of Aluminium 673
Berthelot. Use of Compressed Oxygen in the Calorimetric Bomb . . 673
Naumann (A.). Reconversion of Heat into Chemical Energy by Production of Water and Carbonic Anhydride Generator Gases 673
De Forcrand. Thermochemistry of Sodium Isopropoxide 674
Massol (G.). Tartronic Acid and Alkali Tartronates 675
Scholz (R.). Heat of Dissolution of Salts in Water 676
Dieterici (C.). Theory of Heat of Dissolution and of Osmotic Pressure . 676
Raoult. Freezing Points of Dilute Solutions of Cane-sugar 678
Pickering (S. U.). Cryoscopic Behaviour of Weak Solutions. Part I. Sulphuric Acid 678
Lobry de Bruyn (C. A.). Apparatus for Determining Vapour Pressures . 679
Eiloart (A.). Stereochemical Models of Organic Molecules 679
Noyes (W. A.). Lecture Experiment: Burning Sulphur in Oxygen . . 679
Costa (T.). Refractive Power of Isocyanides and Nitriles 757

PAGE

MAGNANINI (G.). Absorbent Power of Coloured Salts and Electrolytic Dissociation 757
GUYE (P. A.). Molecular Dissymmetry 758
COLSON (A.). Stereochemistry of Diacetyltartaric Acid 758
GUYE (P. A.). Stereochemistry and the Laws of Rotatory Power . . 759
BOUTY (E.). Coexistence of Dielectric Power and Electrolytic Conductivity 759
KOCH (K. R.) and A. WÜLLNER. Galvanic Polarisation at Small Electrodes 759
GOUY. Electrocapillary Phenomena 760
LE CHATELIER (H.). Optical Measurement of High Temperatures . . 761
BECQUEREL (H.). Optical Measurement of High Temperatures . . . 761
CARBONELLI (C. E.). Specific Heat of the Diamond 761
GRIMALDI (G. P.). Measurement of the Specific Heat of Liquids at Temperatures above their Boiling Points under Ordinary Pressures . . . 761
BÉKÉTOFF (N.). Heat of Combination of Bromine and Iodine with Magnesium 762
MASSOL (G.). Heat of Formation of Potassium Tricarballylate . . . 762
MASSOL (G.). Citric Acid 763
STOHMANN (F.) and H. LANGBEIN. Thermochemistry of the Carbohydrates and Polybasic Alcohols and Phenols 763
DIETERICI (C.). Theory of Heat of Solution and of Osmotic Pressure . 765
TRAUBE (J.). Cryoscopic Communications 765
CHARPY (G.). Specific Gravities of Aqueous Solutions 765
SKUBICH. Change of Volume of Solutions of Salts 766
GILBAULT (H.). Compressibility of Saline Solutions 766
LINEBARGER (C. E.). Nature of Colloïd Solutions 766
PICKERING (S. U.). The Recognition of Changes of Curvature by means of a Flexible Lath 767
MULLER (P. T.) and J. HAUSSER. Velocity of Decomposition of Diazo-compounds by Water 768
PARMENTIER (F.). Flameless Incandescence Produced by Coal Gas . . 768
TECLU (N.). New Laboratory Burner 768
BARY (P.). Refractive Indices of Saline Liquids. 929
SCHÜTT (F.). Determination of the Molecular Refraction of Solid Chemical Compounds in Solutions of the same 929
DE BOISBAUDRAN (L. DE). Spectra of Gallium. 930
GORE (G.). Changes of E.M.F. and Temperature by Mixing Electrolytes . 930
ARRHENIUS (S.). Correction in the Calculation of the Heat of Dissociation of Electrolytes 931
BERTHELOT. Persulphuric Acid and its Salts 931
FOGH (J.). Sugars 933
BACH (R.). Thermochemistry of Hydrazine: Molecular Refraction of some Nitrogen Compounds 933
SCHALL (C.). Determination of Vapour Density 934
AMAGAT (E. H.). Determination of the Density of Liquefied Gases and of their Saturated Vapours. 934
WANKLYN (J. A.). Liquid and Gaseous Mixtures 935
PLANCK (M.). Theory of Diffusion and Electrolysis 935
ARRHENIUS (S.). Applicability of Planck's Proof to the Law of Van't Hoff 935
RAOULT (F. M.). Determination of the Freezing Point of very Dilute Solutions 935
BEYERINCK (M. W.) Action at a Distance of Aqueous Solutions on Water Vapour 936
MOORE (B.). Velocity of Reaction in Mixtures of Isohydric and Non-isohydric Solutions of Acids 936
BLÜMCKE (A.). Labile Conditions of Equilibrium in Mixtures of Two Substances at a Temperature below the Melting Point of either . . . 936
LE CHATELIER (H.). Equilibrium of Chemical Systems under Unequal Pressures 937

PAGE

Retgers (J. W.). Influence of Foreign Substances on the Form, Purity, and Size of Crystals Separating from a Solution 937
Adkins (H.). Relations between Atomic Weights 938
Dudley (W. L.). Colours and Absorption Spectra of thin Metallic Films and of Incandescent Metallic Vapours. Electrical Volatility. . . 1037
Chassy (A.). Laws of Electrolysis 1037
Bagard (H.). Thermoelectric Phenomena at the Contact of two Electrolytes 1037
Kümmell (G.). Separation of Precipitates at the Boundary of Electrolytes 1038
Arrhenius (S.). Electrical Conductivity of Substances in Mixed Solvents . 1038
Hinrichs (G.). Mechanical Determination of the Boiling Points of Compounds with Complex Terminal Substitution 1039
Hinrichs (G.). Mechanical Determination of the Boiling Points of Alcohols and Acids. 1039
Stohmann (F.) and C. Kleber. Hydrogenation of Closed Rings: Constitution of Camphoric Acid 1040
De Forcrand. Thermal Function of Phenol 1042
Pickering (S. U.). Heat of Dissolution of Gases in Liquids . . . 1042
Amagat (E. H.). Density of Liquefied Gases and their Saturated Vapours: Critical Constants of Carbonic Anhydride 1043
Barus (C.). Volume Lag and its Bearing on Molecular Constitution . . 1043
Henrich (F.). Absorption Coefficient of Gases 1043
Lauenstein (C.). Viscosity of Aqueous Salt Solutions 1044
Van't Hoff (J. H.). Theory of Solutions 1045
Pickering (S. U.). Cryoscopic Behaviour of Weak Solutions: Parts II, III, and IV. 1045
Pfeiffer (H.). Partially Miscible Solutions 1046
Parmentier (F.). Abnormal Dissolution: Saturated Solutions . . . 1047
Behrend (R.). Solubility of Double Compounds 1047
Retgers (J. W.). Isomorphism 1048
Rimbach (E.). Behaviour of Optically Active Substances in Mixtures of Two Solvents. 1137
Ostwald (W.). Colour of the Ions 1137
Pictet (R.). Physical and Chemical Phenomena at very Low Temperatures 1138
Miolati (A.). Melting Points of Mixtures 1139
Berthelot and Matignon. Heats of Combustion and Formation of Ethyl Alcohol and Formic and Acetic Acids 1139
Massol (G.). Dibromomalonic Acid 1140
Massol (G.). Thermochemistry of Bibasic Organic Acids: Methylmalonic and Methylsuccinic Acids 1140
Massol (G.). Glutaric Acid 1141
Matignon (C.). Substitution of Radicles in Union with Carbon and Nitrogen respectively: Explosives 1141
Matignon (C.). Thermochemistry of Guanidine and Nitroguanidine . 1142
Thomsen (J.). Thermochemistry of Hydrazine and of Hydroxylamine . 1143
Scheurer-Kestner. Formulæ for Calculating the Heating Power of Coal 1143
Colot (E.). Temperature of Saturated Vapours of various Liquids under the same Pressure 1143
Handl (A.) and R. Přibram. Viscosity of Liquids 1143
Planck (M.). Theories of Osmotic Pressure and of Electrolytic Dissociation 1143
Noyes (A. A.). Determination of the Electrolytic Dissociation of Salts by means of Solubility Experiments 1143
Sonnenthal (R. v.). Dissociation of Dilute Solutions of Tartrates . . 1144
Meyerhoffer (W.). Interval of Change 1145
Ostwald (W.). Polybasic Acids 1145
Charpy (G.). Chemical Equilibrium in Solutions 1146
Linebarger (C. E.) Formation of Layers in Solutions of Salts in Mixtures of Water and Organic Liquids 1146

PAGE

HARKER (J. A.). Reaction of Hydrogen with Chlorine and Oxygen . . 1147
SPRING (W.). Equilibrium of Chemical Systems under Unequal Pressures 1148
FREER (P. C.) and F. L. DUNLAP. Hydrolysis of Substituted Ethyl Acetates 1148
LEHMANN (O.). Spheres of Condensation and Evaporation . . . 1149
OSTWALD (W.). Studies on Energetics 1149
PAUL (T.). Apparatus for Hot Filtration 1150
FREER (P. C.). Lecture Experiment illustrating the Effusion of Gases . 1150
MAGNANINI (G.). Influence of Boric Acid on the Electrical Conductivity of Dilute Alcoholic Solutions of Organic Acids 1265
ARRHENIUS (S.). Diffusion in Aqueous Solutions 1265
MOISSAN (H.) and H. GAUTIER. Specific Gravity of Gases . . . 1267
CHABRIÉ (C.). Passage of Substances in Solution through Mineral Filters and Capillary Tubes 1267
HANTZSCH (A.) and A. MIOLATI. Dissociation Constants of Stereoisomeric Nitrogen Compounds 1268
LELLMANN (E.). Affinity Coefficients of Acids 1269
LELLMANN (E.) and J. SCHLIEMANN. Affinity Coefficients of Acids . . 1269
COLLAN (U.). Autocatalysis 1270
FLAVITZKY (F.). Correlation of Oxygen and Hydrogen Compounds of the Elements 1270
GRÜNWALD (A.). Hasselberg's so-called Second or Compound Hydrogen Spectrum, and the Structure of Hydrogen 1381
STREINTZ (F.). Theory of Secondary Batteries 1381
HOLLAND (R. J.). Alteration of the Conductivity of a Solution by the Addition of a Small Quantity of a Non-electrolyte. 1382
PUSCHL (C.). Expansion of Water by Heat 1382
JÄGER (G.). Stochiometry of Solutions 1382
PÉCHARD (E.). Heat of Formation of Permolybdic Acid 1383
TRAUBE (J.). Molecular Volume of Dissolved Substances 1383
TAMMANN (G.). Permeability of Precipitated Membranes 1383
ROOZEBOOM (H. W. B.). Solubility Curves of Pairs of Salts . . . 1384
BEHREND (R.). Solubility of Double Compounds 1385
MORSE (H N.) and J. WHITE. Transportation of Solids in a Vacuum by the Vapours of Metals 1386
BARTHEL (G.). Bunsen Burner for Spirit 1386
SCHULZE (C.) and B. TOLLENS. Simple Apparatus for Evaporating under Reduced Pressure 1386

Inorganic Chemistry.

LUNGE (G.) and L. MARCHLEWSKI. Revised Hydrochloric Acid Tables . 11
MOISSAN (H.). Place of Fluorine in the Classification of the Elements . 11
MOISSAN (H.). Action of Fluorine on Phosphorus Trifluoride . . . 12
BERTHELOT. Persulphates 12
FOCK (A.) and K. KLÜSS. Thiosulphates 12
FOCK (A.) and K. KLÜSS. Ammonium Dithionate Hydrochloride . . 13
LUNGE (G.) and H. REY. Revised Nitric Acid Tables. 13
MAI (J.). Compounds of Sulphur and Phosphorus 14
NURICSÁN (J.). New Method of Preparing Carbon Oxysulphide. . . 15
LEA (M. C.). Allotropic Silver; III. Blue Silver 15
BRÜGELMANN (G.). Characteristics of the Alkaline Earths 17
CHRIST (A.). Composition of a Boiler Incrustation 17
GIORGIS (G.). Action of Hydrogen Peroxide and of Water Saturated with Carbonic Anhydride on Magnesium 17
PRUD'HOMME. Cuprammonium Oxide. 18
CAMMERER. Action of Ferric Chloride on Metallic Sulphides . . . 18
VERNON (H. M.). Manganese Tetrachloride 19

PAGE

OSMOND (F.). Calorimetric Researches on the Condition of Silicon and of Aluminium in Cast Iron. 19
EVANS (W. P.). Attempts to Prepare Metallic Chromium from Chromic Fluoride. 19
CLASSEN (K.). "Pure Bismuth" 20
CARNEGIE (D.). Sulphur Tetroxide 111
CURTIUS (T.). Azoimide 112
MARCHLEWSKI (L.). Colour of Nitric Acid. 113
MOISSAN (H.). Boron Phosphoiodides. 114
WARREN (H. N.). Reducing Action of Graphitoïdal Silicon . . . 115
REICH (K.). Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Solutions of Sodium Chloride 116
LEA (M. C.). Allotropic Silver 116
SCHNEIDER (E. A.). Colloïdal Silver 117
GAUTIER (H.) and G. CHARPY. Direct Combination of Chlorine and Bromine with Metals 118
CHASSEVANT (A.). Lithium Copper Chloride 118
ROUSSEAU (G.). Formation of Saline Hydrates at High Temperatures. . 119
ROUSSEAU (G.). Crystallised Ferric Oxychlorides 119
PFEIFFER (E.). Action of Water on Glass 120
LETEUR. Stannibromides 121
CAUSSE (H.). Dissolution of Bismuth Chloride in a Saturated Solution of Sodium Chloride. Basic Bismuth Salicylate 122
CRISMER (L.). Preparation of Pure Hydrogen Peroxide Solutions . . 270
NEWTH (G. S.). Preparation of Hydrobromic Acid 270
WINKLER (L. W.). Solubility of Gases in Water 271
PICKERING (S. U.). The Densities of Sulphuric Acid Solutions . . . 271
PICKERING (S. U.). Contraction on Mixing Sulphuric Acid and Water . 271
RÜCKER (A. W.). Density and Composition of Dilute Sulphuric Acid. . 271
PICKERING (S. U.). Densities of Sulphuric Acid Solutions. 272
MOISSAN (H.). Boron Phosphides 272
BESSON (A.). Boron Phosphides. 273
BÉKÉTOFF (N.). Influence of Steam and other Gases on the Combustion of Carbonic Oxide and Oxygen 274
D'ARSONVAL (A.). Reactions of Carbonic Anhydride at High Pressures . 274
BÉKÉTOFE (N.). Reduction of Cæsium 274
BÉKÉTOFF (N.). Properties of Cæsium and its Hydroxide 274
JOANNIS. Action of Sodammonium and Potassammonium on Metals . . 275
ENGEL (R.). Influence of Ammonia on the Solubility of Ammonium Chloride. 276
ESSNER (J. C.). Precipitation of Copper by Iron and the Action of Iron on Ferric Solutions. 276
BALESTRA (E.). Mercurammonium Compounds 276
KOHLRAUSCH (F.). Solubility of Glass in Cold Water. 277
ENGEL (R.). Reaction between Potassium Permanganate and Hydrogen Peroxide 277
CAMMERER. Action of Ferric Chloride on Metallic Sulphides . . . 278
ÉTARD (A.). Coloration of Solutions of Cobalt and the State of the Salts in the Solutions 278
BERTHELOT. Oxidation of Nickel Carbonyl. 279
CAVAZZI (A.) and D. TIVOLI. Action of Hydrogen Phosphide on an Ethereal Solution of Bismuth Tribromide 279
ANTONY (U.) and A. LUCCHESI. Auric Sulphide. 280
VÉZES (M.). Iodonitro- and Bromonitro-platinum Compounds . . . 280
SCHNEIDER (E.). Two New Seleno-salts 281
JOLY (A.). Saline Compounds of the Lower Ruthenium Oxides with the Higher Oxides 282
JOLY (A.). Action of Light on Ruthenium Peroxide 282
KREUSLER (U.). Direct Combination of Chlorine with Metals . . . 401
TRAUBE (M.). Sulphuryl Holoxide 401

PAGE

Lobry de Bruyn (C. A.). Free Hydroxylamine 402
Becker (A.). Reduction of Nitric Acid to Ammonia by the Galvanic Current 403
Rammelsberg (C). Hypophosphates 403
Le Chatelier (H.). Metallic Borates. 404
Besson (A.). Silicon Thiochloride 404
Petersen (E.). Allotropic State of some Elements 405
Luzi (W.). Graphite 406
Lewes (V. B.). Analysis of the Products of Incomplete Combustion . . 407
Davies (H. E.). Calcium Phosphate from Solution in Acetic Acid . . 407
Georgievics (G. v.). Action of Carbonic Anhydride and Ferric Hydroxide on Tricalcium Phosphate 408
Kwasnik (H.). Action of Barium Peroxide on Metallic Salts . . . 408
Merz (V.). Magnesium Nitride 409
Aslanoglou (P. L.). Supposed Copper Nitride 409
Granger. Copper Phosphides 410
Veley (V. H.). Chemical Changes between Lead and Nitric Acid . . 410
Weber (R.) and E. Sauer. Composition of Glass suitable for Chemical Utensils 410
Mylius (F.) and F. Foerster. Examination of Glass for Chemical Purposes 411
Recoura (A.). Green Chromic Sulphate 411
Recoura (A.). Isomeric Forms of Chromic Sulphate 411
Neumann (G.). α-Orthostannic Acid 412
Venable (F. P.). Preparation of Pure Zirconium Chloride from Zircons . 412
Causse (H.). Solution of Antimonious Chloride in Saturated Solutions of Sodium Chloride 413
Glatzel (E.). Antimony Thiophosphate 413
André (G.). Bismuthic Acid 413
Barth (K.). Complex Salts of Sulphurous Acid. 564
Ditte (A.). Metallic Borates 565
Luzi (W.). Carbon 565
Scheurer-Kestner. Action of Carbon on Sodium Sulphate in Presence of Silica 565
Ouvrard (L.). Lithium Nitride 565
Maquenne. Direct Combination of Nitrogen with Alkaline Earth Metals . 566
Otto (R.) and D. Drewes. Magnesium Lead Bromide 566
Kwasnik (W.). Action of Ammonia on Cadmium Chloride . . . 566
Neumann (G.) and F. Streintz. Behaviour of Hydrogen towards Lead and other Metals 567
Lachaud and Lepierre. Lead Chromate 567
Lachaud and Lepierre. Thallium Chromate 567
Guntz. Action of Carbonic Oxide on Iron and Manganese 568
Rousseau (G.). Hydrated Potassium Manganites 569
Engel. The Variations in Colour of Cobalt Chloride 569
Potilitzin (A.). The Hydrates of Cobalt Chloride, and their Alterations in Colour 571
Hartley (W. N.). Action of Heat on Solutions of Chromium Salts . . 571
Hillebrand (W. F.) and W. H. Melville. Isomorphous Thorium and Uranous Sulphates 571
Bailey (H.). Alloy of Tin and Sodium 572
Wilm (T.). Palladious Oxide 572
Freyer (F.) and V. Meyer. Boiling Point of Zinc Chloride and Bromide and Ignition Temperature of Electrolytic Gas 680
Hall (W. F.). Action of Nascent Hydrogen and Nascent Oxygen on Nitric Acid 680
Scheurer-Kestner. Decomposition of Sulphurous Anhydride by Carbon at High Temperatures 681
Spring (W.) and E. Bourgeois. Action of Iodine on Sodium Hydrogen Sulphite 681

PAGE

Moissan (H.). Amorphous Boron 681
Moissan (H.). Preparation of Amorphous Boron 682
Lobry de Bruyn (C. A.). Explosion of Ammonium Nitrate . . . 683
Sodeau (W. H.). Silver Sulphite 684
Rousseau (G.) and G. Tite. Silver Nitrosilicate. Existence of a Nitrosilicic Acid 684
Causse (H.). Solubility of Tricalcium Phosphate and Dicalcium Phosphate in Solutions of Phosphoric Acid 684
Maquenne. Barium Carbide 685
Parmentier (F.). Lead Chlorosulphide and Bromosulphide . . . 685
Pesci (L.). So-called Mercurosammonium Compounds 685
Schottländer (P.). Metals of the Cerium Group 686
Lunge (G.). Action of Certain Liquids on Aluminium 687
Pickering (S. U.). Hypothetical Manganese Tetrachloride . . . 687
André (G.). Bismuthic Acid 688
Joly (A.). Ruthenium Chloride and Hydroxychloride 688
Duncan (W.). Solubility of Iodine in Chloroform 769
Senderens (J. B.). Action of Sulphur on Metallic Solutions . . . 770
Crismer (L.). Preparation of Crystallised Hydroxylamine . . . 771
Besson (A.). Combination of Ammonia with Boron Bromide and Iodide . 771
Besson (A.). Carbon Chlorobromides 771
Schneider (A.) and F. W. Clarke. Action of Ammonium Chloride at its Dissociation Temperature on Silicates 772
Johannis. Definite Alloys of Sodium 773
Wells (H. L.) and S. L. Penfield. Salts of Cæsium containing 3 Atoms of Halogen to 1 of Metal 773
Schneider (E. A.). Organosols 775
Schneider (E. A.). Preparation of Pure Colloïdal Silver 775
Béchamp (A.). Action of Light on Silver Chloride 775
Adrian and Bougarel. Separation of Barium from Strontium Salts . 776
Maquenne. Nitrides of Barium and Strontium 776
Seubert (K.) and A. Schmidt. Action of Magnesium on Chlorides . . 776
Buchner (G.). Cadmium Sulphides 778
Remsen (I.). Double Halogen Salts 779
Herty (C. H.). Double Halogen Salts of Lead 779
Gilpin (J. E.). Mercurous Hypochlorosulphite 780
Boisbaudban (L. de). Samarium 780
Saunders (C. E.). Double Halogen Salts of Manganese 780
Poulenc (C.). Nickel Potassium and Cobalt Potassium Fluorides . . 781
Jörgensen (S. M.). Rhodosochromium Salts 782
Jörgensen (S. M.). Constitution of Cobalt, Chromium, and Rhodium Bases 783
Recoura (A.). Chromosulphuric Acid and Metallic Chromosulphates . 783
Piccini (A.). New Series of Fluoroxy-compounds of Molybdenum . . 784
Richardson (G. M.). Double Halogen Salts of Tin 784
Piccini (A.) and G. Giorgis. Fluoroxyvanadates, Fluoroxyhypovanadates, and Fluorvanidites. 785
Saunders (C. E.). Double Halogen Salts of Antimony 788
Brigham (C. P.). Double Halogen Salts of Bismuth 788
Mylius (F.) and F. Foerster. Preparation and Assaying of Pure Platinum 789
Askenasy (P.) and V. Meyer. Slow Combustion of Gaseous Mixtures . 938
Askenasy (P.) and V. Meyer. Photochemical Notes. 939
Emich (F.). Preparation of Nitric Oxide 939
Emich (F.). Behaviour of Nitric Oxide at High Temperatures . . . 940
Emich (F.). Reaction between Nitric Oxide and Oxygen 940
Emich (F.). Action of Potassium Hydroxide on Nitric Oxide . . . 940
Volney (C. W.). Manufacture of Nitric Acid 941
Klobb (P.). Crystallised Anhydrous Sulphates 941
Schneider (E. A.). Colloïdal Silver 941

PAGE

Gorgeu (A.). Decomposition of Silver Permanganate 942
Shields (J.). Occlusion of Hydrogen by Lead 942
Neumann (G.). Behaviour of Copper and of the Noble Metals towards some Gases and Vapours 942
Warren (H. N.). Aluminium Sulphide 943
Lachaud and C. Lepierre. New Iron Salts 943
Cammerer (J. B.). Action of Hydrogen Peroxide on the Oxides of Molybdenum, Tungsten, and Vanadium 944
Schneider (R.). Reduction of Potassium Platinum Thiostannate: Potassium Thioplatinosate 944
Delépine. Alcoholic Solutions of Ammonia 1049
Schützenberger (P.). Compounds of Carbon and Silicon. . . . 1050
Tammann (G.). Metaphosphates 1050
Newbury (S. B.). Copper Sulphites 1051
Weber (R.) and E. Sauer. Composition of Glass suitable for Chemical Purposes. 1052
Schjerning (H.). Manganese Compounds 1052
Terne (B). Iron in Bone-black 1053
Gal (J.). Formation of Plastic Sulphur from Sulphur Vapour . . . 1150
Přiwoznik (E.). Formation of Sulphuric Acid by burning Illuminating Gas 1151
Wislicenus (W.). Synthesis of Hydrogen Nitride 1151
Sabatier (P.) and J. B. Senderens. Action of Nitric Oxide on Metals and Metallic Oxides 1151
Besson (A.). Phosphorus Chloronitride and Phosphamide . . . 1152
Moissan (H.). Amorphous Boron 1153
Moissan (H.) Boron Iodide 1154
Bodländer (G.). Behaviour of Molecular Compounds on Dissolution . 1154
Barthe (L.). Strontium Phosphate 1156
Riban (J.). Basic Zinc Nitrate 1156
Rousseau (G.) and G. Tite. Cadmium Hydrosilicate 1157
Rousseau (G.) and G. Tite. Basic Nitrates 1157
Brun (E.). Compounds of Cuprous Iodide and Ammonium Thiosulphate . 1157
Nickel (E.). Graphical Chemistry of Glass 1158
Schützenberger (P.). Nickel 1158
Poulenc (C.). Nickel and Cobalt Fluorides 1159
Péchard (E.). Permolybdates 1160
Kehrmann (F.) and M. Freinkel. Complex Inorganic Acids. Phosphotungstic Acids 1160
Lazareff (P.). Mutual Displacement of Haloïds 1270
Leduc (A.). Composition of Water and Gay-Lussac's Law of Volumes . 1271
Baubigny (H.) and E. Péchard. Efflorescence of Metallic Sulphates . 1271
Sabatier (P.) and J. B. Senderens. Action of Nitric Oxide on Metallic Oxides 1271
Rousseau (G.) and G. Tite. Decomposition of Basic Nitrates by Water . 1272
Besson (A.). Phosphorus Bromonitride 1272
Rauter (G.). Silicon Tetrachloride 1273
Wiesner (J.). Examination of Different Forms of Carbon . . . 1273
Pratesi (L.). Supersaturated Aqueous Solutions of Carbonic Anhydride . 1274
Potilitzin (A.). Lithium Bromate 1275
Chassevant (A.). Double Chlorides of Lithium and Metals of the Magnesium Series 1275
Potilitzin (A.). Rate of Decomposition of Calcium Chlorate by Heat . 1275
Werner (A.). Basic Calcium Nitrate 1276
Weber (R.). Influence of the Composition of the Glass of Slides and Cover Glasses on the Durability of Microscopic Objects . . . 1276
Kouklin (E.). Action of Potassium Sulphate on Strontium Carbonate . 1276
Barthe and Falières. Preparation of Pure Strontium Salts . . . 1277
Kuriloff (V.). Action of Hydrogen Peroxide on the Hydrated Oxides of Cadmium, Zinc, and Magnesium 1278

PAGE

Montemartini (C.). Action of Nitric Acid on Metals 1278
Montemartini (C.). Action of Nitric Acid on Zinc 1279
Gröger (M.). A New Oxyiodide of Lead 1280
Pionchon (J.). Specific Heat and Latent Heat of Fusion of Aluminium . 1281
Balland. Aluminium 1281
Buisine (A.) and P. Buisine. Utilisation of Burnt Pyrites in the Manufacture of Iron Salts 1281
Lachowicz (B.). Dissociation of Ferric Phosphate in presence of Water and of Saline Solutions 1282
Lepierre (C.) and Lachaud. Nickel and Cobalt 1282
Péchard (E.). Permolybdic Acid 1283
Vèzes (M.). Nitrogen Compounds of Platinum 1283
Vèzes (M.). Chlorazopalladium Compounds 1284
Fink (E.). Phosphopalladious Compounds 1285
Antony (U.). Removal of Platinum from Iridium 1285
Stortenbecker (H.). Compounds of Chlorine with Iodine . . . 1387
Tavel (E.) and A. Tschirch. Iodine Trichloride 1388
Ditte (A.). Iodic Acid and its Salts 1388
Leduc (A.). Atomic Weight of Oxygen 1388
Schmitz-Dumont (W.). Insoluble Sulphur 1389
Přiwoznik (E.). Formation of Sulphuric Acid and Ammonium Sulphate by Burning Coal Gas 1389
Traube (W.). The Amides and Imides of Sulphuric Acid 1389
Sabatier (P.) and J. B. Senderens. Action of Nitric Peroxide on Metals and Metallic Oxides 1390
Lobry de Bruyn (C. A.). Free Hydroxylamine 1391
Moissan (H.). Boron Trisulphide 1392
Moissan (H.). Boron Pentasulphide 1394
Luzi (W.). Artificial Corrosion of the Diamond 1394
Feit (W.) and K. Kubierschky. Extraction of Rubidium and Cæsium Compounds from Carnallite 1395
Morse (H. N.) and H. C. Jones. Redetermination of the Atomic Weight of Cadmium 1397
Williams (G. H.). Crystals of Metallic Cadmium 1398
Granger. Mercury Phosphide 1398
Klobb (T.). Mineralising Action of Ammonium Sulphate 1399
Guillemin (G.). Micrographic Analysis of Alloys 1399
Bettendorff (A.). Earths of the Cerium and Yttrium Groups . . 1400
Foerster (F.). Action of Superheated Water and Solutions of Alkalis and Salts on Glass 1401
Chorley (J. C.). Slag from the Manufacture of Phosphorus in Electrical Furnaces 1401
Montemartini (C.). The Reaction between Nitric Acid and Metals . . 1402

Mineralogical Chemistry.

Stone (G. H.). Asphalt of Utah and Colarado 21
Pirsson (L. V.). Gmelinite from Nova Scotia 21
Brackett (R. N.) and J. F. Williams. Newtonite and Rectorite, two new Minerals of the Kaolin Group 22
Eakins (L. G.). Astrophyllite and Tscheffkinite 22
Iddings (J. P.) and S. L. Penfield. Minerals in Hollow Spherulites of Rhyolite 23
Giorgis (G.). Siliceous Sand of Monte Soratte 23
Le Chatelier (H.). Reproduction of Acid Rocks 23
Davidson (J. M.). Kamacite, Tænite, and Plessite from the Welland Meteoric Iron 24
Weed (W. H.). A Gold-bearing Hot-spring Deposit 24
Paternò (E.). Hot Mineral Spring at Sclafani 25

PAGE

MALLARD and E. CUMENGE. Boléite 123
LASPEYRES (H.). Polydymite, Ullmanite, and Wolfsbergite . . . 124
DIETZE (A.). New Chilian Minerals, Darapskite, Lauarite, Iodochromite . 124
KENNGOTT (A.). Formula of Axinite 125
CLARKE (F. W.) and E. A. SCHNEIDER. Constitution of certain Micas, Vermiculites, and Chlorites 125
KIMBALL (J. P.). Genesis of Iron Ores by Replacement of Limestone . 126
BAUER (M.). Basalt of the Stempel, near Marburg 126
WEED (W. H.) and L. V. PIRSSON. Sulphur, Orpiment, and Realgar in the Yellowstone Park 283
ATHERTON (T. W. T.). Occurrence of a Natural Gold Sulphide . . . 283
HILLEBRAND (W. F.). New Analyses of Uraninite 283
FOOTE (A. E.). Discovery of Diamonds in Meteoric Iron 284
BAILEY (E. H. S.). The Tonganoxie Meteorite 284
ESSNER (J. C.). Composition of some Natural Subterranean Waters near Port-Vendres 285
JOLY (J.). Determination of the Melting Point of Minerals . . . 414
HUNT (T. S.). Natural Classification of Minerals 415
KOENIG (G. A.). Paramelaconite and Footeite 415
HILLEBRAND (W. F.). Samarskite from Colorado 416
BODLÄNDER (G.). Formation of Melilite during the Burning of Portland Cement 416
RINNE (F.). Relations between Minerals of the Heulandite and Desmine Groups 417
KENNGOTT (A.). Formulæ of Vesuvian Minerals 417
FIRTSCH (G.). Rumpfite 417
KISLAKOWSKY (E. D.). Meteorite of Turgaisk 418
DAMBERGIS (A. K.). Mineral Springs of Edepsos 418
ROOZEBOOM (H. W.). Waters of the North Sea 419
SCHÖNFLIES (A.). Theories of the Structure of Crystals 572
HARRINGTON (B. J.). So-called Amber of Cedar Lake, Canada . . . 573
PRENDEL (R.). Tourmaline from Siberia 573
JOHNSTONE (A.). Action of Water on Mica 573
CANZONERI (F.). Hot Mineral Spring at Finca Huracatao, Salta, Argentine 574
ALEXÉEFF (W.). Elaterite and Dopplerite 689
DI BOCCARD (G.). Manganese Hydroxide from the Euganeen, Italy . . 689
ZEMJATSCHENSKY (P. A.). Iron Ores of Central Russia 689
TJELOUCHIN (W.). Vivianite 690
LUZZATO (G.). Natrolite from Monte Baldo 690
MELNIKOFF (M. P.). Zoisite from Orenburg 690
MATTIROLO (E.). Breithauptite from Sarrabus, Sardinia 790
BLEICHER. Microscopic Structure of the Oölitic Iron Ore of Lorraine . 791
DUNNINGTON (F. P.). Distribution of Titanic Oxide on the Earth's Surface 791
FEIT (W.). Heintzite 791
LUEDECKE (O.). Heintzite 791
FEIT (W.). Ascharite, a New Borate 792
LUEDEKING (C.) and H. A. WHEELER. Barytes from Missouri . . . 792
LUEDEKING (C.). Synthesis of Crocoïte and Phœnicrocoïte . . . 792
GENTH (F. A.). Hübnerite, Hessite, Bismutite, and Natrolite . . . 793
FARRINGTON (O. C.). Chemical Composition of Iolite 793
LANE (A. C.), H. F. KELLER, and F. F. SHARPLESS. Chloritoïd, Grünerite, and Riebeckite from Michigan 793
CLARKE (F. W.). Tschermak's Theory of the Chlorite Group and its Alternative 794
VAN HISE (C. R.). Iron Ores of the Marquette District, Michigan . . 794
FOOTE (A. E.). New Meteoric Iron from Maryland 794
KUNZ (G. F.) and E. WEINSCHENK. Aërolite from Kansas 795
LOSANITSCH (S. M.). Meteorite of Jelica 795
FRESENIUS (R.). Julianen and Georgen Springs at Eilsen 796

PAGE

Luzi (W.). Allotropism of Amorphous Carbon 945
Clarke (F. W.). Fractional Analysis of Silicates 945
Mallard. Native Iron from Cañon Diablo. 947
Daubrée. Native Iron from Cañon Diablo. 947
Loczka (J.). Hungarian Minerals 1054
Lavenir (A.). Martite 1055
Kunz (G. F.). Brookite, Octahedrite, Quartz, and Ruby 1055
Carnot (A.). Fluorine in Natural Phosphates 1055
Pisani (F.). Cuprodescloizite from Mexico. 1055
Treadwell (F. P.). Milarite 1056
Rinne (F.). Gismondine from Westphalia 1056
Kakuchi (Y.). Cordierite as Contact Mineral 1056
Lacroix (A.). Fouqueite, a New Mineral 1056
Smyth (C. H.). Peridotite in Central New York. 1057
Gill (A. C.). Minerals from the Chrome Iron Ore Deposits of Maryland . 1057
Terreil (A.). Chromiferous Clay from Brazil 1057
Merrill (G. P.) and R. L. Packard. Azure-like Pyroxenic Rock from New Mexico 1057
Adams (F. D.). Mellitite-bearing Rock from Canada 1058
Montemartini (C.). Serpentine Rock from Borzanasca 1058
Ramsay (W.) and H. Berghell. Rock of the Jiwaara, in Finland . . 1058
Hunter (M.) and H. Rosenbusch. Monchiquite, a Rock of the Eleæolite Syenite Class 1058
Huntington (O. W.). The Prehistoric and Kiowa Co. Pallasites . . 1059
Kunz (G. F.). Meteoric Iron from Colfax Township, North Carolina . . 1059
Kunz (G. F.). Meteoric Iron from Ferguson, North Carolina . . . 1059
Doss (B.). Meteorite of Misshof, Kurland, Russia 1059
Nordenskiöld (O.). The Ljungby Meteorite 1060
Duparc (L.) and A. Delebecque. Waters and Basins of the Lakes of Aiguebelette, Paladru, Nantua, and Sylans 1061
Carnot (A.). Fluorine in Recent and Fossil Bones 1161
Duboin (A.). Artificial Reproduction of Leucite 1161
Parmentier (P.). Preservation of Mineral Waters 1162
Zaloziecki (R.). Glauber's Salt in the Potash Mines of Kalusz . . . 1286
Duboin (A.). Artificial Formation of Potassium-nepheline . . . 1286
Thoulet (J.). Water from the Arctic Ocean 1287
Parmentier (F.). Aluminium in Mineral Waters 1287
Spica (P.). The Mineral Water of Monte di Malo 1287
Riban (J.). Alteration of Chalybeate Mineral Waters 1288
Parmentier (F.). Chalybeate Mineral Waters 1289
Riban (J.). Chalybeate Mineral Waters 1289
Warren (H. N.). New Silver Ore 1404
Igelström (L. J.). Jacobsite and Braunite from Sweden 1404
Flink (G.). Braunite and Friedelite from Sweden 1405
Penrose (R. A. F.). Limonite in Texas 1405
Sandberger (F. v.). Minerals from the Fichtelgebirge 1406
Eakins (L. G.). Triplite and Kaolin from the United States . . . 1406
Zinkeisen (H.). Manganese Spar and Celestine from Scharfenberg . . 1406
Melville (W. H.) and W. Lindgren. Minerals from the Pacific Coast . 1407
Widman (O.). Thaumasite, Wollastonite, Chabasite, and Vesuvian . . 1407
Nordenskiöld (G.). Pholidolite 1408
Wülfing (E. A.). The Pyroxene Family 1408
Chatard (T. M.). Analysis of Pyroxene 1409
Münster (C. A.). Garnierite from Norway 1409
Nordenström (G.). Allanite from Gyttorp, Sweden 1409
Blomstrand (C. W.). Gadolinite 1410
Petersson (W.). Gadolinite 1410
Kengott (A.). Formula of Tourmaline 1410
Vogt (J. H. L.). Composition of Melilite 1410
Clarke (F. W.). Petalite, Spessartine, and Willemite 1411

PAGE

HAMBERG (A.). Minerals from the Harstigen Mine, Sweden . . . 1411
KALECSINSZKY (A.). Helvine from Hungary 1412
BRAUNS (R.). Products of the Weathering of Diabase 1412
LINDGREN (W.). Analcime as a Rock-forming Mineral 1413
CARNOT (A.). Proportion of Fluorine in Fossil Bones of Various Ages . 1413
HOWELL (E. E.). New Meteorites 1413

Organic Chemistry.

HOLLEMANN (A. F.). Constitution of Mercuric Fulminate 25
LIPPMAN (F.). Constitution of Allyl Cyanide 27
HENRY (P.). Direct Synthesis of Primary Alcohols 27
WAGNER (G.). Oxidation of Tertiary Alcohols 28
BERTRAND (G.). Xylose 28
BERTRAND (G.). Constitution of Xylitol and Xylose 29
SCHIFF (R.). Epichloramine 29
PAAL (C.) and A. HEUPEL. Unsaturated Fatty Amines 30
SCHINDLER (T.). Crotonaldoxime 32
SCHIFF (R.) and N. TARUGI. Oximes of Chloral and Butylchloral . . 33
NASINI (R.) and T. COSTA. Sulphinic Derivatives and their Analogies with Compounds of Aromatic Amines 34
WAGNER (G.). Oxidation of Mixed Fatty Ketones 35
RÖHMANN (F.) and W. SPITZER. Determination of the Affinity of Organic Acids by Means of Lacmoid 37
KACHLER (J.). Behaviour on Dry Distillation of the Silver Salts of Organic Acids 37
KWISDA (A.). Action of Hydriodic Acid on Amido-Acids 38
GLÜCKSMANN (C.). β-Trimethylethylidenelactic Acid. 38
CONRAD (M.) and C. BRÜCKNER. Halogen Derivatives of Malonic Acid . 39
MICHAEL (A.). Action of Zinc on Ethyl Dibromosuccinate 40
CLAUS (A.). Decomposition of Glutaric Acid at a High Temperature . . 40
AUWERS (K.), E. KÖBNER, and F. v. MEYENBURG. Synthesis of Polybasic Fatty Acids 41
DEUTZMANN (A.). Furfurylamine 43
WIDMAN (O.). Intramolecular Change of the Propyl Group 43
SEŃKOWSKI (M.). Isomeric Change in the Synthesis of Aromatic Amines and Phenols 44
KRAUS (A.). Action of Nitrous Acid on Resorcinol Diethyl Ether and on Triethylresorcinol 44
KOWALSKI. Hydroxyquinones 45
TIEMANN (F.). Isoeugenol, Diisoeugenol, and their Derivatives . . . 45
TIEMANN (F.). Oxidation Products of Safrole 46
RABAUT (C.). Action of Benzyl Chloride on Orthotoluidine 48
LAUTH (C.). Oxidation of Azo-compounds 48
SEYEWETZ (A.). Action of Phenylhydrazine on Phenols 49
WISLICENUS (W.) and M. SCHEIDT. Combination of Phenylhydrazine with Ethyl Oxalacetate 49
CLAUS (A.). Oximes and so-called Stereochemistry 50
BEHREND (R.). Intramolecular Change of some Isaldoxime Derivatives . 50
LOSSEN (W.). Amidines 51
STEWART (A.). Thio-derivatives of Orthamidobenzamide 54
BÖTTINGER (C.). Condensation of Anilpyruvic Acid 54
POLIKIER (H.). Tartranilide 54
LOSANITSCH (S. M.). Aromatic Dithiocarbamates 55
BIGINELLI (P.). Ethyl Acetoacetate Aldehydeuramides 56
LÖW (M.). Ethylation of Salicylaldehyde 57
NAGAI (W. N.). Pæonol 58
TIEMANN (F.). Pæonolphenylhydrazone and Oxime 59
TIEMANN (F.). Acetovanillone 59

PAGE

NEITZEL (E.). Derivatives of Diacetovanillone 61
OTTO (T.). Synthesis of Acetovanillone from Guaiacol and Acetic Acid . 61
CRÉPIEUX (P.). Aromatic Hydroxyketones 62
CIAMICIAN (G.) and P. SILBER. Constituents of Paracoto Bark . . . 62
TIEMANN (F.). Vanilloylcarboxylic Acid 64
HINSBERG (O.). Benzenesulphamides and Mixed Secondary Amines . . 64
POLIKIER (H.). Synthesis of Indole from Tartaric Acid and Aniline . . 66
ZATTI (C.) and A. FERRATINI. Molecular Weight of Nitrosoindole . . 67
PAAL (C.). Indazole Derivatives 67
HEYMANN (H.). Synthesis of Indigodisulphonic Acid 69
ABENIUS (P. W.) and H. G. SÖDERBAUM. Diphenyltetraketone . . 69
CIAMICIAN (G.). Constitution of Naphthalene 69
KÜHLING (O.). Azines of the Uric Acid Group 70
PEACOCK (J. C.). Volatile Oil from *Aristolochia reticulata* . . . 70
POMERANZ (C.). Bergaptene, the Stearoptene of Bergamot Oil . . . 71
HALLER (A.). Action of Sodium Alkyloxides on Camphor: Preparation of Alkyl Camphors 72
MINGUIN (J.). Action of Sodium Benzyloxide on Ethyl Camphocarboxylate 74
ZANETTI (C. U.). Determination of the Constitution of the Homologues of Pyrroline 74
HEUSER (A.) and C. STOEHR. Methyldipyridyls 75
EINHORN (A.). Preparation of α- and β-Pyridyllactic Acid from α-Picoline 75
CONRAD (M.) and L. LIMPACH. Synthesis of Quinoline Derivatives by means of Alkyl Acetoacetates 78
HANRIOT. Action of Hydroxylamine on Ketonic Nitriles 79
PAAL (C.) and F. KLECKE. Methylphenyldihydroquinazoline and its Derivatives 80
LIPPMANN (E.) and F. FLEISSNER. Action of Hydriodic Acid on Quinine . 81
SKRAUP (Z. H.). Compounds of the Cinchona Alkaloïds with Hydriodic Acid 83
MARINO-ZUCO (F.). New Alkaloïd from Chrysanthemum Flowers . . 84
DEMME (W.). New Albumin from Protoplasm 86
DENIGÈS (G.). Preparation of Bromoform from Acetone and Sodium Hydrobromite. 126
REBOUL (E.). Bromobutylenes 127
TOLLENS (B.) and P. WIGAND. Penterythritol, a Tetrahydric Alcohol . 127
BAUER (R. W.). Sugar from Quince-juice 128
HOFFMEISTER (W.). Cellulose Gum 129
CROSS (C. F.) and E. J. BEVAN. Constitution of the Lignocelluloses . . 129
GABRIEL (S.). Thio-derivatives of Ethylamine 130
GABRIEL (S.). δ-Chlorobutylamine: Synthesis of Pyrrolidine . . . 131
FREUND (M.) and F. SCHÖNFELD. Action of Nitrous Acid on Nonylamine . 132
MALBOT (H.) and A. MALBOT. Formation of Tetralkylammonium Iodides . 133
PUM (G.). Benzoyl Derivatives of Glucosamine 134
SCHIFF (R.). Chloralimide 134
TIEMANN (F.). Amidoximes and Azoximes 135
GARNY (F.). Action of Hydroxylamine on Derivatives of Succinic and Glutaric Acids 136
MODEEN (H.). Action of Hydroxylamine on Ethyl Cyanacetate . . . 139
OBERMÜLLER (K.). Saponification with Sodium Ethoxide 139
LOSSEN (W.) and G. VOSS. Metallic Formates 140
GAZE (R.). Propionates 140
NEF (J. U.). Ethyl Acetoacetate 140
ERDMANN (H.). Condensation of Levulinic Acid with Aldehydes . . 147
WISLICENUS (W.). Reduction of Ethyl Oxalacetate 147
PECHMANN (H. v.) and K. JENISCH. Reduction of Acetonedicarboxylic Acid 147
PECHMANN (H. v.) and K. JENISCH. Alkylacetonedicarboxylic Acids . . 148

PAGE

Hinsberg (O.). Behaviour of certain Ketonic Acids towards Hydrogen Sodium Sulphite 148
Salzer (T.). Alkali Citrates 149
Formánek (E.). Formation of Uric Acid from Cyanacetic Acid and Carbamide 149
Markwald (W.), M. Neumark, and H. Stelzner. Hydantoïns, and Bases derived from them 149
Laves (E.). Chemical and Physiological Relations of Sulphones . . . 153
Angeli (A.). Ethyl Acetothienoncoxalate 154
MacKerrow (W.). Bromine Carriers. 155
Kraemer (G.) and A. Spilker. Condensation Products of Allyl Alcohol with Methylbenzenes 156
Mazzara (G.) and G. Plancher. Bromo-derivatives of Carvacrol . . 156
Bamberger (E.), B. Berlé, and L. Strasser. Behaviour of Carvacrol towards Reducing Agents 157
Gabriel (S.). Preparation of Primary Amines by means of Potassium Phthalimide 157
Kinzel (W.). Oxidation Products of Paramidophenetoïl 158
Van Romburgh (P.). Action of Nitric Acid on Dimethylorthanisidine . 159
Autenrieth (W.) and O. Hinsberg. Phenacetin: Methoxyorthophenylenediamine 160
Pechmann (H. v.) and K. Jenisch. Action of Diazobenzene on Acetonedicarboxylic Acid 161
Pechmann (H. v.) and K. Jenisch. Action of Phenylhydrazine on Acetonedicarboxylic Acid 162
Bamberger (E.). Symmetrical Bisphenylhydrazone of Mesoxaldehyde . 162
Mai (J.). Action of Oximes on Diazo-compounds 163
Behrend (R.). Molecular Transformation of the Aldoximes . . . 163
Nietzki (R.). Synthesis of Wesclsky's Resorcinol-blue 163
Paschkowezky (S.). Aromatic Secondary Chlorocarbamides and Tetrasubstituted Carbamides 164
Tiemann (F.). Reduction of Aromatic Aldehydes 167
Harries (C. D.). Reduction of Salicylaldehyde. 168
Harries (C. D.). Methyl Orthohydroxycinnamyl Ketone and its Derivatives 169
Beckmann (E.) and T. Paul. Action of Sodium on Ketones and Aldehydes 169
Claus (A.) and A. Reh. Bromination of Bromobenzoic Acids . . . 171
Claus (A.) and N. Davidsen. Nitration of Orthochloroparatoluic Acid . 172
Claus (A.) and P. Böcher. Nitration of Metachloroparatoluic Acid . . 173
Claus (A.) and J. Herbabny. Nitration and Bromination of Orthobromoparatoluic Acid 174
Claus (A.) and R. Seibert. Dibromoparatoluic Acid. 176
Claus (A.) and J. Joachim. Nitration of Orthonitroparatoluic Acid . . 176
Claus (A.) and C. Beysen. Dinitroparatoluic Acids and their Derivatives. 177
Dittrich (M.). and V. Meyer. Derivatives of Ethyl Dinitrophenylacetate 178
Gabriel (S.) and G. Cohn. Diphenylmaleïc Anhydride 178
Lossen (W.) and C. Rahnenführer. Composition and Crystalline Form of Barium Isophthalate 179
Goldschmiedt (G.). Opianic Acid 179
Allendorff (O.). Oximes of Opianic and Phthaldehydic Acids . . 180
Rossin (O.). Metahemipinic Acid 180
Böttinger (C.). Derivatives of Tannin 181
Fischer (P.). Chloronitrobenzenesulphonic Acids 182
Täuber (E.). Diphenyleneazone 183
Baumann (E.) and M. Klett. Stilbene, Thionessal, and Tolane Sulphide 184
Herzberg (W.) and M. Polonowsky. Action of Nitrous Acid on Tetramethyldiamidobenzophenone 185
Koller (G.). Derivatives of Paraphenylbenzophenone 186
Auwers (K.) and V. Meyer. Claus' Theory of the Benzileoximes . . 186
Noelting (E.). Dyes of the Triphenylmethane Group 187
Donner (A.). Benzeneazo-α-Naphthylglycocine 191

PAGE

BAEYER (A. v.), R. SCHODER, and E. BESEMFELDER. Hydronaphthoic Acids 191
WITT (O. N.) and H. KAUFMANN. α-Naphthol-α-sulphonic Acid . . 194
WITT (O. N.) β-Naphthaquinonesulphonic Acids 196
PICTET (A.) and H. J. ANKERSMIT. Phenanthridine 196
PICTET (A.) and S. EHRLICH. Methylphenanthridine and Chrysidines . 197
BOUCHARDAT (G.) and J. LAFONT. Action of Benzoic Acid on Turpentine 199
BRÜHL (J. W.). Terpenes and their Derivatives 200
ECKART (U.). German and Turkish Rose Oil 203
BAMBERGER (M.). Natural Resins 204
GOLDSCHMIEDT (G.) and R. JAHODA. Substance contained in the Petals of *Gentiana verna*. 205
LIECHTI (R.). Rind of *Garcinia mangostana* 205
MICHAELIS (L.). Nicotenylamidoxime 206
PECHMANN (H. v.) and O. BALTZER. α-Pyridone 208
SCHMIDT (A.) and G. WICHMANN. Piperazine 210
BÖTTIGER (E.). Quinolinehydrazines 212
GABRIEL (S.) and P. ELFELDT. μ-Phenylpentoxazoline 212
ELFELDT (P.). Oxazolines and Pentoxazolines 213
SPICA (P.) and G. CARRARA. Thiazole Compounds 215
GABRIEL (S.) and R. JANSEN. Quinazolines 217
SCHMIDT (E.). Choline 219
KRÜGER (M.). Adenine 219
BRUHNS (G.) and A. KOSSEL. Adenine and Hypoxanthine . . . 220
HESSE (O.). Behaviour of Cupreïne and Quinine with Methyl Iodide . 221
LIPPMANN (E.). Preparation of Homologues of Quinine 222
HESSE (O.). Isocinchonine 222
JUNGFLEISCH (E.) and E. LEGER. Isocinchonines 222
HOUDAS (J.). Digitaleïne 222
FREUND (M.) and C. DORMEYER. Hydrastine 223
SIEBERT (C.). Lupanine, the Alkaloïd of the Blue Lupine 223
MALFATTI (H.). Nucleïns 224
CHABRIÉ (C.). New Proteïd from Human Blood Serum 224
WILDERMANN (M.). Method for Determining the Constitution of Saturated and Unsaturated Halogen Derivatives and Hydrocarbons . . . 285
GUARESCHI (I.). Platinum Thiocyanate and Platinothiocyanates . . 286
COQUILION and HENRIVAUX. Decomposition of Hydrocarbons with Steam 288
VESTERBERG (A.). Hydrocarbons from α- and β-Amyrin 288
SEELIG (E.). Derivatives of Glycerol 288
TOLLENS. Reactions of Xylose and Arabinose 290
VESTERBERG (A). Oxidation Products of the Amyrins 290
HERZFELD (A.). Pectin Substances 291
HOFFMANN (E.) and V. MEYER. First Product of the Reduction of Nitro-compounds with Tin and Hydrochloric Acid or with Stannous Chloride. 291
MINUNNI (G.). Isomerism of Oximes 291
HECTOR (D. S.). Action of Oxidising Agents on Aliphatic Thiocarbamides. 292
BÉHAL (A.). Constitution of Caprylaldehyde 293
KOENIGS (W.). Dry Distillation of Organic Silver Salts 293
GOLDBERG (G.), P. KUNZ, and K. KRAUT. Glycocine and its Derivatives . 294
DUVILLIER (E.). Diethylamidocaproic Acid 294
MELIKOFF (P.) and P. PETRENKO-KRITSCHENKO. Derivatives of Isocrotonic Acid 295
PECHMANN (H. v.) Preparation of Dehydracetic Acid 296
LINOSSIER (G.). Resolution of Inactive Lactic Acid by *Penicillium glaucum* 297
LOSSEN (W.). Decomposition of Glutaric Acid at a High Temperature . 297
DELISLE (A.). Conversion of Unsaturated Acids into their Stereochemical Isomerides by Soda 297
MELIKOFF (P.) and P. PETRENKO-KRITSCHENKO. αβ-Dimethylglyceric Acid from Angelic Acid 297
MENOZZI (A.) and G. APPIANI. Derivatives of Glutamic Acid . . . 298
FISCHER (E.). New Isomeride of Galactonic Acid and of Mucic Acid . 299

PAGE

TIEMANN (F.). Constitution of the Hydroxamic Acids 300
DAVIES (S. H.). Alkyl and Acidyl Sulphides 300
BAUMANN (E.) and E. FROMM. Thio-derivatives of Furfuraldehyde . . 301
CIAMICIAN (G.) and A. ANGELI. Constitution of Tetrole Nuclei . . 302
SALVATORI (S.). Derivatives of Ethyl Acetothienoneoxalate . . . 303
ANGELI (A.). Use of Sodium Hypophosphite in Sandmeyer's Reaction . 305
LOBRY DE BRUYN (C. A.). Displacement of the Nitro-group by Chlorine . 305
DACCOMO (G.). Dithiocarbonic Acids 306
DACCOMO (G.). Metachlorothiophenol 306
DACCOMO (G.). Ortho- and Para-chlorothiophenol 307
HEIBER (F.). Action of Methylchloroform and Ethylchloroform on Alkaline Solutions of Phenols 308
MAZZARA (G.) and G. PLANCHER. Derivatives of Carvacrol . . . 309
NIETZKI (R.) and B. SCHÜNDELEN. Action of Dinitrochlorobenzene on Polyhydric Phenols 310
WAGNER (G.). Oxidation of Aromatic Compounds containing the Side Chain C_3H_5 310
SEMMLER (F. W.). Myristicin and its Derivatives 311
KÜHN (B.) and J. RIESENFELD. Action of Carbonyl Chloride on Benzylamine 312
HANTZSCH (A.). Nomenclature of Stereoisomeric Nitrogen Compounds and of Rings containing Nitrogen 312
RABAUT (C.). Action of Benzyl Chloride on Ortho- and Para-toluidine . 313
JABLIN-GONNET. Action of Benzyl Chloride on Metaxylidine . . . 314
FEITH (E.) and S. H. DAVIES. Action of Hydroxylamine on Acetomesitylene 314
NIETZKI (R.) and H. KAUFMANN. Derivatives of Trinitroquinol . . . 314
SAUNDERS (C. E.). Diazobenzene Perbromide 316
LELLMANN (E.) and B. ARNOLD. Intramolecular Formation of an Azo-group 316
KOTHE (R.). Alkyl Derivatives of Hydroxylamine 316
TIEMANN (F.). Amidoximes and Azoximes 317
MARCUS (E.). Nitrogenous Derivatives of some Aromatic Dihydroxyaldehydes 317
GOLDBECK (O.). Nitrogenous Derivatives of Parahomosalicylic Acid . . 318
PASCHEN (E.). Derivatives of Orthohomosalicylaldehyde and of Orthohomoparahydroxybenzaldehyde 320
RICHTER (E.). β-Trichloro-α-hydroxypropenylamidoxime 321
RUSSANOW (A.). Phenylglyoximes 321
TIEMANN (F.). Action of Nitrous Acid on Benzenylamidethoxime . . 323
GRAWITZ (S.). Dyeing with Aniline Black in the Dry Way . . . 323
PASCHKOWEZKY (S.). Thiophenylcarbamides 324
OBRÉGIA (A.). Action of Potassium Cyanide on Halogen Derivatives of Ketones 324
GROHMANN (A.). Action of Ammonia and Aniline on Halogen Substituted Nitrobenzoic Acids 326
GARELLI (F.). Oximes of Some Ketonic Acids 327
FEITH (E.). Derivatives of Mesitylene 329
ALDRINGEN (F.). Thiocoumarin and its Analogues 329
FISCHER (P.). Action of Ammonia and Aniline on Negatively Substituted Halogenised Benzenesulphonic Acids 331
WEGE (H.). Acetoximes 333
FRANKE (E.). Action of Sulphonic Chlorides on Orthamidobenzamide . 334
SCHÖPFF (M.). Displacement of Halogen Atoms in the Benzene Ring . 335
SCHÖPFF (M.). Friedel-Craft's Synthesis 337
WEGE (H.). Deoxybenzoin 338
HANTZSCH (A.) and F. KRAFT. Stereochemical Isomerism of Nitrogen Compounds 338
GOLDBERG (B.). Formation of Rosaniline 340
MEYER (V.) and H. WEGE. New Method of Formation of Desaurins . 340

PAGE

Fischer (O.) and E. Hepp. Studies in the Induline Group . . . 341
Volpi (A.). Homologues of Acridine 342
Bizzarri (D.). Methylcarbazacridine 343
Zinsser (F. J.). Aromatic Nitriles 344
Cleve (T. P.). 1 : 3 : 4-Dichloronaphthalenesulphonic Acid . . . 344
Cleve (T. P.). Amidonaphthalenesulphonic Acid 345
Hoffmann (O.). Nitrosonaphtholsulphonic Acids 346
Linebarger (C. E.). Hydroxyanthranol 346
Elbs (K.). Paranthracene 347
Brühl (J. W.). Terpenes and their Derivatives 347
Crismer (L.). Crystalline Products from Lemon and Bergamot Oils . . 349
Oglialoro (A.) and O. Forte. Action of Hydriodic Acid and Amorphous Phosphorus on Picrotin 349
Thoms (H.). Constituents of the Buds of *Chrysanthemum cinerariæfolium* 349
Kruskal (N.) and R. Kobert. *Agrostemma githago* (Corn Cockle) . . 350
Zanetti (C. U.). Constitution of the Ethylpyrrolines 350
Foerster (F.). Derivatives of Carbonyl Chloroplatinites 352
Claus (A.) and H. Howitz. Action of Bromine on Para- and Ortho-hydroxyquinoline 353
Schotten (C.) and W. Schlömann. Oxidation of Piperidine and Tetrahydroquinoline Derivatives 354
Michaelis (A.) and O. Lampe. Synthesis of Phenylpyrazolidine . . 355
Will (W.). Osazone of Hydroxypyruvic Acid 356
Pellizzari (G.). Phenylguanazole 356
Merling (G.). Tropine 358
Cazeneuve (P.). A Violet from Codeïne 360
Giesel (F.). Alkaloïd from Javan Coca Leaves 361
Kobert (R.). Cyanomethæmoglobin and Detection of Hydrogen Cyanide . 362
Patein (G.). Transformation of Albumin 362
Fleurent (E.). Ammonio-copper Ammonium Cyanide 420
Lespieau (R.). Dibromopropylene 420
Cazeneuve (P.). Formation of Acetylene from Bromoform . . . 421
Kuntzmann (M.). Preparation of Cuprous Acetylide 421
Delmont (L.). Action of Alkali Sulphides on Chloroform 421
De Forcrand. Disodium Glycol 421
Gernez (D.). Compounds of Sorbitol and Perseïtol with Molybdic Acid . 422
Gunning (J. W.). Preparation of Raffinose from Molasses . . . 422
Lösekann (G.). Formaldehyde 423
Haubner (G.). Action of Sulphurous Anhydride on Crotonaldehyde . . 424
Démètre-Vladesco. Action of Chlorine on Ketones of the Fatty Series . 424
Pechmann (H. v.). Preparation of Fatty 1 : 2-Diketones 425
Hantzsch (A.). Configuration of Fatty Ketoximes 426
Schleicher (B.). α-Bromisovaleric Acid : Pimelic Acid : Synthesis of Teraconic Acid 427
Kleinstück (O.). Specific Gravity of Japan Wax 428
Holt (A.). Stereoisomeric Relations of Erucic and Brassidic Acids . . 429
Garzarolli-Thurnlackh (K.). γ-Trichloro-β-hydroxybutyric Acid. New Synthesis of Malic Acid 429
Zelinsky (N.). Stereoisomeric Dimethyladipic Acids and Dimethylpimelic Acids 430
Fleischhauer (H.). Condensation of Cyanides with Ethereal Salts . . 431
Bruck (P.). Diiodoacetylenedicarboxylic Acid and Diiodoacrylic Acid . 431
Pechmann (H. v.). Ethyl Acetonedicarboxylate 431
Volhard (J.). Hydrochelidonic Acid or Acetonedicetic Acid . . . 432
Volhard (J.). Phenylhydrazonehydrazide of Levulinic Acid . . . 436
Zelinsky (N.). Stereoisomerism of Dimethyldihydroxyglutaric Acid . 436
Fischer (E.) and O. Piloty. New Pentonic Acid and the Second Inactive Trihydroxyglutaric Acid 437
Langlet (N. A.). Action of β-Iodopropionic Acid on Ethyl Thiocarbamate 440

PAGE

KURNAKOW (W.). Silver Compound of Thiocarbamide 441
KÖHLING (O.). Alloxanhydrazone 442
KEHRER (E. A.). Condensation of Levulinic Acid with Furfuraldehyde . 442
THIELE (A.). β-Isopropylthiophen 442
KONOVALOFF. Action of Dilute Nitric Acid on Nononaphthene . . . 443
WITT (O.). Derivatives of Paranitrorthochlorobenzyl Bromide . . . 444
KOENIGS (W.) and R. W. CARL. Condensation of Isoamylene and Cinnamene with Phenols 446
LIMPACH (L.). Synthesis of the Sixth Dihydroxytoluene 447
ANGELI (A.). Action of Nitrous Acid on some Unsaturated Aromatic Compounds 447
ZINCKE (T.) and O. FUCHS. Hexachloroparadiketohexene 447
LELLMANN (E.). Metachloroparacetotoluidide 450
BURNS (P. S.). Dimolecular Nitriles 450
CURTIUS (T.) and H. LANG. Substitution of the Azo-group for Ketonic Oxygen 451
WILLGERODT (C.) and E. G. MÜHE. Derivatives of Phenylhydrazine . 453
CURTIUS (T.) and L. PFLUG. Secondary Asymmetrical Hydrazines . . 456
WISLICENUS (W.) and M. SCHEIDT. Action of Phenylhydrazine on Ethyl Ethoxyoxalacetate 458
HEUSLER (F.). Action of Acetic Anhydride on Diazoamido-compounds . 458
LIEBERMANN (C.). Heat developed in the Isomeric Change of the Oxime of Opianic Anhydride 459
TIEMANN (F.). Action of Benzenesulphonic Chloride on Amidoximes . . 460
PINNOW (J.). Action of Benzenesulphonic Chloride on Amidoximes . . 460
TIEMANN (F.). Preparation of Benzenylhydrazoximamidobenzylidene . 461
LOSSEN (W.). Constitution of the Hydroxamic Acids 461
TIEMANN (F.). Constitution of the Hydroxamic Acids 461
WERNER (A.). Stereoisomeric Derivatives of Benzhydroxamic Acid . . 461
BERTRAM (A.). Phenylthiocarbamide and Imidothiocarbamates . . . 465
THIESING (H.). Methylenedibenzamide 467
KOSSEL (A.). Derivatives of Phenylamidoacetic Acid 467
LIEBERMANN (C.). Stereoisomeric and Polymeric Cinnamic Acids . . 469
LIEBERMANN (C.) and H. SACHSE. Diiodocinnamic Acid 470
GÖTTIG (C.). Isomeric Dichlorhydrin Metahydroxybenzoate . . . 471
TIEMANN (F.). Phenyl-α-hydroxycrotonic Acid 471
BIEDERMANN (J.). Derivatives of Phenyl-α-hydroxycrotonic Acid . . 471
BIEDERMANN (J.). New Method of preparing the Amide, Anilide, and Phenylhydrazide of Mandelic Acid. 473
RUHEMANN (A.). Paraxylalphthalide 473
LIMPRICHT (H.). Preparation of Nitrososulphonic Acids 475
SCHMIDT (M.). Action of Sulphurous Anhydride on Isonitroso-Compounds 476
OTTO (R.) and A. BÖSSING. Aromatic Thiosulphonic Acids. . . . 478
HAUSSER. Nitrosulphobenzoic Acid 479
LIEBERMANN (C.) and F. DICKHUTH. Acetylhydrindigotin and Acetylindigotin 479
TÄUBER (E.). Synthesis of Diamidocarbazole 480
TÄUBER (E.). Diphenylenazine 482
COHN (G.). Benzaldiphenylmaleïde and its Derivatives 482
SMITH (A. W.). Influence of Substituting Radicles on the Configuration of Aromatic Ketoximes 487
ISTEL (E.). Indulines 492
WICHELHAUS (H.). Methylnaphthalenes 492
SCHERLER (O.). Action of Chlorine and of Nitric Acid on Methylnaphthalenes 493
BAMBERGER (E.) and M. KITSCHELT. Action of Hypochlorous Acid on β-Naphthaquinone 494
LEROY (J. A.). Action of Phosphoric Chloride on Methyl Naphthyl Ketones 495
REISSERT (A.). Julole. 496

PAGE

Reissert (A.). Dyes obtained from Ketomethyljuloline and Methylepidone 498
Wallach (O.). Derivatives of Carvole 499
Wallach (O.). Menthylamine 500
Friedel (C.). Ethyl Camphorates and Isocamphorates 500
Kiliani (H.). Digitonin 501
Jorissen (A.) and E. Hairs. Linamarin 502
Schall (C.) and C. Dralle. Oxidation of Brasilin. New Derivatives of Resorcinol 502
Soxhlet (V. H.). Preparation of Flavin 503
Kostanecki (S. v.) and B. Nessler. Hydroxyxanthones 504
Hemmelmayr (F. v.). Base obtained from Pyridine 504
Busch (A.) and W. Koenigs. Synthesis of β-Chloroquinaldine . . . 505
Ganelin (S.) and S. v. Kostanecki. Constitution of Orthohydroxyazo-dyes 506
Claisen (L.). Isoxazoles 506
Stoehr (C.). Dimethyldiazine 507
Freund (M.) and others. Biazolones 508
Hesse (O.). Quinine Hydrochlorides 514
Pum (G.). Action of Hydriodic Acid on Cinchonine 514
Hesse (O.). Sulphonic Acids of Cinchona Alkaloïds 514
Hofmeister (F.). Crystalline Egg-albumin 515
Drechsel (E.). Decomposition of Albumin. 515
Wildermann (M.). Exchange of Chlorine, Bromine, and Iodine between Inorganic and Organic Haloïd Compounds 574
Konovaloff. Nitration of Hydrocarbons of the Methane Series . . 575
Meyer (V.). Aliphatic Nitro-compounds 575
Varet (R.). Action of Ammonia on Mercuric Cyanide and its Haloïd Derivatives 575
Meyer (E. v.). Polymerisation of the Nitriles 576
De Forcrand. Thermal Value of the Hydroxyl Groups in Glycol . . 576
Kronstein (A.). Preparation of Symmetrical Tribromhydrin . . . 577
Meyer (V.) and F. Müller. Substitution in the Aliphatic Series . . 577
Petit (P.). Production of Dextrin 577
Rouvier (G.). Fixation of Iodine by Starch 578
Paal (C.). Unsaturated Aliphatic Amines 578
Pellizzari (G.). Nitroguanidine 579
Pulvermacher (G.). Reaction of Trithioformaldehyde and Formaldehyde 579
Schindler (T.). Crotonaldoxime and Allyl Cyanide 580
Salzer (T.). Water of Crystallisation. 581
Davies (S. H.). Alkyl and Acidyl Sulphides 581
Stiassny (E.). Preparation of Methylpropylacetic Acid 581
Gérard (E.). Derivatives of Daturic Acid 582
Arnaud (A.). New Acid of the $C_nH_{2n-4}O_2$ Series 582
Brühl (J. W.). Ethyl Acetoacetate 583
De Varda (G.). Nitro-derivative of Methyl α-Hydroxypropionate . . 583
Papasogli (G.). Cotton-seed Products 584
Feist (F.). Dehydracetic Acid 584
Feist (F.). Dehydracetic Chloride 587
Feist (F.). Constitution of Dehydracetic Acid 587
Fauconnier (A.). Action of Phosphoric Chloride on Ethyl Oxalate . . 588
Sonnenthal (S.). Dissociation in Dilute Solutions of Tartrates . . . 588
Ordonneau (C.). Cause of Acidity of Grapes: Tartromalic Acid . . 589
Wislicenus (W.). β-Methylmalic Acid 589
Michael (A.) and O. Schulthess. Additive Products of Ethyl Sodaceto-acetate and Sodiomalonate with Ethereal Salts of Unsaturated Acids . 590
Camps (R.). Trimethylenetrisulphone. 591
Camps (R.). Trimethylenedisulphonesulphide 592
Meunier (J.). Reduction of Benzene Hexachloride 594
Schöpff (M.). Friedel-Crafts Synthesis 594
Willgerodt (C.). First Reduction Products of the Nitro-group . . 594

PAGE

Fileti (M.) and V. Abbona. Propoxy-derivative of Cumonitrile . . 595
Mazzara (G.). Bromamidocarvacrol 595
Nietzki (S.) and L. Kurtenacker. Penta-derivatives of Benzene . . 596
Bladin (J. A.). Condensation Products of Dicyanophenylhydrazine with Aliphatic Aldehydes 596
Bladin (J. A.). Action of Ethyl Acetoacetate on Dicyanophenylhydrazine 597
Auwers (K.) and V. Meyer. Stereoisomeric Nitrogen Compounds other than Oximes 598
Claus (A.). Oximes and the so-called Stereochemistry 598
Schiff (U.) and A. Vanni. Amidotolyloxamic and Urethanotolyloxamic Acids 599
Meyer (V.). Commercial Benzoic Chloride. 604
Hoffmann (E.) and V. Meyer. Benzoyl Compounds 604
Filetti (M.) and L. Boniscontro. Oxidation Products of Paradibromohomocumic Acid 604
Errera (G.) and G. Baldracco. Paramethylhydratropic Acid. . . . 605
Pratesi (L.). Action of Nitric Acid on Phenylglycollic Acid . . . 607
Niementowski (S. v.). α-Methylphthalic Acid 607
Ikuta (M.). Action of Ethyl Acetoacetate on Quinone. Synthesis of Benzofurfuran Derivatives 608
Laves (E.). Trithiorthoformates. 611
Laves (E.). Formation of Trisulphones from Disulphones 613
Zatti (C.) and A. Ferratini. Action of Methyl Iodide on α-Methylindole 614
Mazzara (G.) and A. Leonardi. Carbazole 616
Bizzari (D.). Carbazacridines. Dehydration of Amides in contact with Diphenyl Derivatives 617
Gram (J.). Paradiamidodiphenylmethane 618
Chalanay (L.) and E. Knoevenagel. Dicyanostilbene 618
Chalanay (L.) and E. Knoevenagel. Stereoisomeric Diphenylsuccinonitriles 619
Bertoni (G.) and M. Zenoni. Metanitro- and Paranitro-diparadihydroxytriphenylmethane 620
Siboni (G.). Condensation Products of Nitrobenzaldehydes with Hydroxybenzenes 621
De Varda (G.). Condensation of Nitrobenzaldehydes with Salicylic Acid . 621
Bertoni (G.). Metanitrophenylsantoninmethane 622
Orndorff (W. R.) and M. Cauffman. Decomposition of some Diazocompounds of Nitronaphthalenes with Alcohol 622
Otto (R.) and A. Rössing. Tautomerism of Sulphinic Acids . . . 623
Lespieau (R.). Picene 623
Brühl (J. W.), H. Biltz, A. Cantzler, and L. Reuter. Terpenes and their Derivatives 623
Brühl (J. W.). Terpenes and their Derivatives 624
Eckart (C. U.). German and Turkish Rose Oils 625
Kuriloff (B.). Terpenes from the Resin of *Pinus abies* 625
Koenigs (W.) and A. Eppens. Camphorone 626
Barbier (P.). Puleone, an Isomeride of Camphor 627
Koerner (G.) and P. Biginelli. Fraxin and Fraxetin 628
Stoehr (C.). Pyridine and Piperidine Bases of the β-Series . . . 628
Stoehr (C.) and M. Wagner. $\beta\beta$-Dimethyldipyridyl. 629
Decker (H.). So-called γ-Bromoquinoline 630
Bamberger (E.) and J. Lorenzen. Benzimidazoles 631
Bamberger (E.) and B. Berlé. Benzimidazoles 632
Dennstedt (M.). Étard's Glycoline and Stoehr's Dimethyldiazine . . 633
Garzino (L.). Tetrahydropyrazine 633
Lederer (L.). Synthesis of Pyrazolone Derivatives 634
Andreocci (A.). Synthesis of 1 : 3-Phenylpyrrodiazolecarboxylic Acid, 3-Methylpyrrodiazole, 3-Pyrrodiazolecarboxylic Acid, and Pyrrodiazole. 636
Bladin (J. A.). Triazole Derivatives 637

PAGE

Otto (R.) and A. Holst. Ethyl and Methyl Morphine Carbonates . . 638
Lippmann (E.) and F. Fleissner. Action of Hydriodic Acid on Cinchonine 639
Schubert (A.) and Z. H. Skraup. Action of Hydriodic Acid on Quinine and Quinidine. 640
Rüdel (C.). Alkaloïds of *Berberis aquifolium* and *B. vulgaris* . . . 641
Beckurts (H.) and P. Nehring. Constituents of Angostura Bark . . 642
Harnack (E.). Ash-free Albumin 645
Vignon (L.). Rotatory Powers of Various Silks 645
Seidel (P.). Fulminuric Acid 690
Grosjean (L.). Decylene and its Derivatives 691
De Forcrand. Sodium Isopropoxide 691
Mixter (W. G.). Decomposition of Ethereal Nitrates by Alkaline Solutions 692
Cross (C. F.) and E. J. Bevan. Cellulose 693
Hantzsch (A.). Aliphatic Stereoisomeric Glyoximes 693
Koenigs (W.). Condensation of Chloral with Ketones 694
Krafft (F.) and A. Beddies. Action of Bromine on the Higher Fatty Acids 695
Wanklyn (J. A.) and W. Johnson. Alde-acids 696
Pechmann (H. v.). Introduction of Acid Radicles into Ethyl Acetoacetate 696
Haller (A.) and A. Held. Haloïd Derivatives of Ethyl Acetoacetate . 697
Hantzsch (A.) and H. Schiffer. Constitution of Ethyl Chloracetoacetate 697
Hjelt (E.). Allylethylsuccinic Acid and Allylmethylsuccinic Acid . . 697
Böttinger (C.). Dimethylracemic Acid 698
Miolati (A.). New Method of Preparing Fatty Hydroxamic Acids . . 698
Hantzsch (A.). Action of Hydroxylamine on Chloral 699
Cramer (C.). Oxamidoacetic Acid 699
Krafft (F.) and E. Bourgeois. Imidosulphonic Acids 700
Comstock (W. J.) and H. L. Wheeler. Alkyl Derivatives of Isosuccinimide 701
Hecht (O.). Thiocarbamides, Cyanocarbamides, and Cyanothiocarbamides. 702
Hecht (O.). Thiobiurets 703
Willgerodt (C.). Metadinitrobenzene 704
Schlieper (F. W.). Reduction of Metabromonitrophenol 704
Dieckmann (W.). Amidine Picrates 705
Prud'homme and C. Rabaut. Conversion of Aromatic Amines into the Chlorine Derivatives of the Hydrocarbons 705
Comstock (W. J.) and H. L. Wheeler. Anilides, Isoanilides, and their Analogues 705
Comstock (W. J.) and R. R. Clapp. Derivatives of Aromatic Formyl Compounds 707
Knorr (L.). Acetoacetanilide 708
Knorr (L.) and H. Taufkirch. β-Methylamidocrotonanilide . . . 708
Tafel (J.). Colour Reactions of Acid Anilides 709
Autenrieth (W.) and O. Hinsberg. Derivatives of Orthotoluylenediamine 709
Claisen (L.). Mixed Azo-compounds 710
Mai (J.). Action of Hydroxylamine on Diazobenzene and Paradiazotoluene Chlorides 710
Tafel (J.). Acid Hydrazides 710
Lossen (W.). So-called Physically Isomeric Hydroxylamine Derivatives . 711
Van Romburgh (P.). Action of Nitric Acid on Alkyl Phenylcarbamates . 711
Kraft (F.) and H. Karstens. Diparatoluamide and Diorthotoluamide 712
Eitner (P.). Action of Sulphuric Anhydride on Nitriles 713
Hough (O.). Iodation of Parabromobenzoic Acid: Salts of Parabromometanitrobenzoic Acid 714
Markovnikoff (F.). Hydrobenzoic Acids 714
Feith (E.). Methyl Mesitylenecarboxylate 715

PAGE

Göttig (C.). Dichlorhydrin Parahydroxybenzoate 715
Hjelt (E.). Orthohydroxymethylbenzoic Acid 715
Schiffer (H.). Derivatives of Gallic Acid and of Pyrogallol . . . 715
Trimble (H.). Chestnut-wood Tanuin 716
Gabriel (S.). ε-Chloramylamine and Synthesis of Piperidine . . . 717
Noelting (E.). Nitration of Butyltoluenesulphonic Acid and Butylxylene-sulphonic Acid 718
Kopp (K.). Substitution Products of Stilbene and Thionessal . . . 718
Linebarger (C. E.). Action of Benzene on Benzal Chloride in presence of Aluminium Chloride 719
Zincke (T.). Action of Bleaching Powder and of Hypochlorous Acid on Quinones and Diketones 720
Seidel (P.). Sulphonic Acids obtained from 1 : 4-Amidonaphthol . . 721
Witt (O. N.). Sulphonic Acids of Amido-α-naphthol and α-Naphthaquinone 722
Linebarger (C. E.). Reaction between Triphenylmethane and Chloroform in presence of Aluminium Chloride 722
Brühl (J. W.) and F. Müller. Terpenes 722
Andres (G.) and A. Andréeff. Russian Peppermint Oil and Menthylamine 723
Oddo (G.). Camphor Group 724
Oddo (G.). Stereochemistry of the Camphor Group 724
Oddo (G.). Camphor Group 724
Michaud (G.). Sapotin : A Glucoside 724
Mai (J.) and K. Aschoff. Preparation of Collidine 725
Hoogewerff (S.) and W. A. Van Dorp. γ-Amidoquinoline . . . 725
Simon-Thomas (J. C. A.). Attempted Synthesis of a Nitramine of the Quinoline Group 725
Noelting (E.) and E. Trautmann. Derivatives of the Methylquinolines and of Metadimethylquinoline 726
Decker (H.). Some Ammonium Compounds 729
Pictet (A.) and S. Popovici. Pyrogenic Synthesis of Isoquinoline . . 730
Jandrier (E.). Nitro-derivative of Antipyrine 730
Brühl (J. W.). Alcohol of Antipyrine 730
Knorr (L.) and P. Duden. Pyrazole Derivatives 731
Autenrieth (W.) and O. Hinsberg. Hydroxyquinoxalines and Ethoxyquinoxalines 732
Busch (M.). Synthesis of Phenotriazines 734
Bladin (J. A.). Triazole 735
Bamberger (E.) and L. Seeberger. Synthesis of Closed Chains . . 735
Bamberger (E.) and W. Dieckmann. Synthesis of Guanamine. . . 736
Bamberger (E.) and W. Dieckmann. Biguanide 737
Jahns (E.). Alkaloïds of the Areca Nut 737
Lassar-Cohn. Cholic Acid and Dehydrocholic Acid 741
Rösing (E.). Oxidation of Albumin in presence of Sulphur . . . 741
Hinrichs (G.). Boiling Points of Paraffin Derivatives 797
Besson (A.). Carbon Chlorobromides 797
Brochet (A.). Pyrogenic Hydrocarbons in Compressed Gas . . . 797
Varet (R.). Action of Metals on Salts dissolved in Organic Liquids . . 797
Hofmann (A. W. v.). Polymeric Methylthiocarbimide 798
Christensen (O. T.). Derivatives of Chromium Ammonium Thiocyanate. 798
De Forcrand. Value of the Primary Alcoholic Function 799
Otto (R.) and A. Rössing. Preparation and Properties of Bunte's Salt (Ethyl Thiosulphate) 799
Meslans (M.). Fluorhydrins from Glycerol 799
De Forcrand. Monosodium Mannitol 800
Gernez (D.). Rotatory Power of Compounds of Perseïtol with Sodium Hydrogen and Ammonium Hydrogen Molybdate 800
Lindsey (J. B.) and B. Tollens. Dextrose from Sulphite Cellulose and from Fir Wood 801

PAGE

Nasini (R.) and V. Villavecchia. Specific Rotatory Power of Cane Sugar in Dilute Solutions 801
Rouvier (G.). Combination of Starch with Iodine 801
Lindsey (J. B.) and B. Tollens. Wood-Sulphite Liquor and Lignin . 802
Winterstein (E.). Vegetable Amyloïd 803
Chancel (F.). Propylamines and their Derivatives 804
Berg (A.). Action of Sodium and Potassium Cyanide on Chlorodiamylamine 804
Schmidt (E.). Preparation of Pure Trimethylamine from Crude Trimethylamine Hydrochloride 805
Malbot (H.) and A. Malbot. Action of Isobutyl Iodide on Trimethylamine 805
Malbot (H.) and A. Malbot. Action of Isoamyl Iodide on Trimethylamine 805
Malbot (H.) and A. Malbot. Action of Capryl Iodide on Trimethylamine 806
Bode (J.). Derivatives of Neurine and Choline 806
Schmidt (E.). Action of Hydriodic Acid and of Hydrobromic Acid on Neurine and Choline 808
Étard (A.). Formation of Bromaldehydes and Bromoketones by the action of Bromine on Alcohols of the Ethyl Series 809
Muller (J. A.). Preparation of Crotonaldehyde 809
Muller (J. A.). Occurrence of a Tetracarbon Aldehyde in a Brandy . 810
Démètre-Vladesco. Action of Chlorine on some Fatty Ketones . . 810
Feist (F.). Chlorinated Diacetylacetone 811
Lieben (A.). Dry Distillation of Silver Salts of Organic Acids . . . 811
Saytzeff (A.). Stereoisomerism of Oleïc and Elaïdic Acids . . . 812
Holt (A.). Stereometric Relations of Erucic and Brassidic Acids . . 812
Fittig (R.). Lactonic Acids, Lactones, and Unsaturated Acids . . . 812
Fittig (R.) and K. T. Ström. Action of Sodium Ethoxide on Butyrolactone 813
Fittig (R.) and W. D. Hoeffken. Divalolactone 814
Fittig (G.) and G. Parker. Condensation of Pyruvic Acid with Dicarboxylic Acids 814
Söderbaum (H. G.). Action of Hydroxylamine on Dibromopyruvic Acid . 815
Pechmann (H. v.). Constitution of Ethyl Acetoacetate and of the so-called Ethyl Formylacetate 816
Haller (A.) and A. Held. Ethyl Bromacetoacetate and Cyanacetoacetate 818
Hantzsch (A.). So-called Ethyl Carbacetoacetate 819
Juillard (P.). Turkey-red Oil 819
Hell (C.) and R. Poliakoff. Amido- and Anilido-derivatives of Succinic Acid 819
Buchner (E.). Fermentation 820
Giustiniani (E.). Action of Heat on the Hydrogen Malates of Methylamine and Benzylamine 820
Genvresse (P.). Synthesis of Tartaric Acid 822
Fischer (E.) and R. S. Curtiss. Optically Isomeric Gulonic Acids . . 822
Buchner (E.) and H. Witter. Citric Acid 824
Buchner (E.) and H. Witter. Symmetrical Ethanetetracarboxylic Acid . 824
Fischer (E.) and J. Hertz. Reduction of Mucic Acid 824
Lindsey (J. B.) and B. Tollens. So-called Artificial Pectic Acid from Fir Wood 827
Buchner (E.) and A. Papendieck. Bromacetamide 827
Guareschi (I.). γ-Substituted Hydantoïns: Carbamido-acids . . . 827
Quenda (E.). γ-Substituted Hydantoïns 828
Crismer (L.). Formation of Hydroxamic Acids of the Fatty Acids by means of Acid Anhydrides 828
Volhard (J.). Compounds of Thiophen and of its Homologues and of some Ketones with Mercuric Chloride 828
Gerlach (M.). β-Ethylthiophen and Thiophen-$\alpha\beta$-dicarboxylic Acid. . 829

PAGE

Douglas (P.). Nitrogenous Derivatives of Thiophen and Furfuran . . 831
Liebermann (C.) and F. Dameröw. Silver Phenylacetylide . . . 831
Gattermann (L.) and A. Cantzler. Aromatic Isocyanates . . . 832
Schimmel. Constitution of Betel Oil 833
Baeyer (A. v.). Quinitol, the Simplest Sugar of the Inositol Group . . 833
Hantzsch (A.). Decomposition Products of Anilic Acid 834
Landolt (H., jun.). Action of Halogens on Chloranilic and Bromanilic Acids 834
Turner (C.). Preparation of Orthonitraniline 837
Niementowski (S.). Anhydro-compounds 837
Gattermann (L.) and O. Neuberg. Synthesis of Dehydrothiotoluidine . 839
Jacobsen (O.) and W. Fischer. Reduction Products of Azo-compounds . 839
Gattermann (L.) and R. Hölzle. Replacement of the Hydrazine Group by Halogens 842
Gattermann (L.), E. S. Johnson, and R. Hölze. Acid Hydrazides . . 843
Fromm (E.). Phenyldithiobiuret 844
Tahara (Y.). Orthohydroxyacetophenone 844
Garelli (F.). Derivatives of Cyanacetophenone 845
Nagai (W. N.). Dehydrodiacetylpæonol 845
Tahara (Y.). Constitution of Dehydrodiacetylpæonol and of Dehydrodiacetylresacetophenone 846
Aschan (O.). Hydrobenzoic Acid 847
De Coninck (O.). Reactions of Isomeric Amidobenzoic Acids 847
Liebermann (C.) and W. Scholz. Formation of Allocinnamic Acid from Phenylpropiolic Acid 848
Liebermann (C.) and A. Hartmann. Condensation of Cinnamic and Allocinnamic Acids 848
Buchner (E.) and H. Dessauer. Phenyltrimethylenecarboxylic Acids . 849
Laves (E.). Sulphones 850
Hinsberg (O.). Benzenesulphonitramide 850
Bogdanowska (V.). Dibenzyl Ketone and Dibenzylcarbinol . . . 851
Perrier (G.). Metaphenyltoluene 851
Löwenherz (R.). Dimetaditolyl 852
Täuber (E.). Formation of an Orthamidoditolylamine from Parahydrazotoluene 853
Barsilowsky (J.). Condensation of Aldehydes with Azo-compounds . 854
Vogtheer (H.). Action of Paramidodimethylaniline on Ketones . . 854
Caro (N.). Hydroxyaurines and their Carboxylic Acids 855
Bamberger (E.) and M. Kitschelt. Action of Hypochlorous Acid on Naphthaquinone 857
Zincke (T.) and T. Arnst. Tetrachlororthodiketohydronaphthalene, its Hydrates and Alcoholates 858
Zincke (T.). Action of Bleaching Powder and Hypochlorous Acid on Quinones 859
Hell (C.) and R. Poliakoff. Action of α- and β-Naphthylamine on Ethyl Bromosuccinate 860
Grandmougin (E.) and O. Michel. Homonucleal Amidonaphthols and Related Derivatives 861
Witt (O. N.) and C. Schmidt. Products of the Reduction of Alkylated Azo-colours of the Naphthalene Series 862
Graebe (C.) and E. Gfeller. Oxidation of Acenaphthene 863
Lauth (C.). Preparation of β-Alizarinamide 864
Collie (J. N.). Constitution of Turpentine and Camphor 864
Berkenheim (A.). Menthol 866
Semmler (F. W.) and F. Tiemann. Oxygen Compounds of Ethereal Oils 868
Wallach (O.). Camphene and Camphoric Acid 868
Gucci (P.) and G. Grassi-Cristaldi. Derivatives of Santonin . . . 869
Ciamician (G.) and P. Silber. Constituents of Coto Bark . . . 873
Pohl (J.). Aristolochin 874

PAGE

Etard (A.). The Chlorophyllic Substances of the Pericarp of the Grape . 874
Heermann (P.). Organic Phosphorus Compounds 875
Widman (O.). Nomenclature of Compounds containing Nitrogenous Nuclei 875
Claus (A.). γ-Bromoquinoline 875
Claus (A.), A. Howitz, C. Massan, and G. Raps. Halogen Alkyl Compounds of Hydroxyquinolines 876
Decker (H.). Action of Alkalis on Alkyl Iodides of the Quinoline and Acridine Series 879
Walter (G.). Oxidation of Benzoyltetrahydroquinaldine, and Nitro-derivatives of the same 881
Bamberger (E.) and M. Kitschelt. Preparation of Isoquinoline from Naphthalene 882
Kaiser (W.) and A. Reissert. Julole 883
Alvisi (U.). Formation of Pyrazole Derivatives from the Dichlorhydrins and Tribromhydrins 884
Balbiano (L.). Platinum Compounds derived from the Pyrazoles . . 885
Georgescu. Tetrahydroketoquinoxalines 886
Möhlau (R.). Oxazine Dyes 887
Kehrmann (F.) and J. Messinger. So-called Dinitrosoazobenzene . . 889
Kehrmann (F.) and J. Messinger. Nomenclature of Rings, consisting of 2 Carbon and 3 Nitrogen Atoms 889
Lellmann (E.) and B. Arnold. Substance containing a Ring of 18 Members 890
Krüger (M.). Adenine 890
Liebermann (L.) and L. Limpach. ψ-Tropine and some ψ-Tropeïnes . 891
Grimaux (E.) and A. Arnaud. Conversion of Cupreïne into Quinine . 892
Freund (M.) and W. Rosenstein. Cinchonine 892
Soldaini (A.). Alkaloïds of *Lupinus albus* 892
Spehr (P.). Ephederine from *Ephedra monostachia* 893
Battandier (J. A.). Glaucine 893
Hesse (O.). *Aristolochia argentina* 894
Arata (P. N.) and F. Canzoneri. "Pillijan" (*Lycopodium saururus*) . 894
Paal (C.). Peptone Salts from Glutin 895
Fermi (C.). Solubility of Fibrin 897
Griffiths (A. B.). Hæmocyanin 898
Heim (F.). Blue Colouring Matter in the Blood of Crustaceæ . . . 898
Hinrichs (G.). Boiling Point Curves of the Normal Paraffins . . . 947
Hinrichs (G.). Mechanical Determination of the Boiling Points of Compounds with Simple Terminal Substitution 948
Hinrichs (G.). Establishment of Fundamental Formulæ for the Calculation of Moments of Inertia 948
Schall (C.). Composition of Ant Oil 948
Schmoeger (M.). Acetylated Lactose and the Optically Different Modifications of Lactose 948
Schmidt (E.) and J. Weiss. Allyltrimethylammonium Chloride and Iodide 949
Schmidt (E.) and A. Partheil. Derivatives of Allyltrimethylammonium Hydroxide 950
Prelinger (O.). Picric Acid as a Reagent for Guanidine 950
Franchimont (A. P. N.). Action of Nitric Acid on the Amidines . . 951
Ludwig (E.). Action of Sulphuric Acid on Methylethylacraldehyde . . 951
Franchimont (A. P. N.). Acetaldoxime 951
Erlenbach (A.). Preparation of Symmetrical Dichloracetone . . . 952
Rügheimer (L.) and E. Mischel. Diamidoacetone 952
Richards (T. W.). Cuprammonium Acetobromide 953
Freer (P. C.). Ethyl Acetoacetate 953
Erlenbach (A.). Action of Sodium on Ethyl Chloracetate 953
Fittig (R.). Lactonic Acids, Lactones, and Unsaturated Acids . . . 956
Fittig (R.) and E. Kochs. Oxidation of Crotonic Acid and Isocrotonic Acid 957
Fittig (R.) and R. Ruer. Oxidation of Ethylcrotonic Acid 958

PAGE

Fittig (R.) and K. Urban. Oxidation of Allylacetic Acid 958
Fittig (R.) and J. Hillert. Oxidation of Hydrosorbic Acid . . . 959
Fittig (R.). Decomposition of Dibromides of Unsaturated Acids by Warm Water and by Dilute Alkalis 959
Fittig (R.) and K. Urban. Decomposition of Dibromovaleric Acid . . 960
Fittig (R.) and J. Hillert. Decomposition of Dibromocaproic Acid . 960
Fittig (R.) and M. C. Clutterbuck. Tetrolic Acid 961
Fittig (R.) and C. Christ. Some new Lactones 962
Pawlewski (B.). Ethyl Chlorocarbonate 963
Volhard (J.). Preparation of Maleïc Anhydride 963
Wislicenus (W.). β-Methylmaleïc Acid 963
Marchlewski (L.). Aqueous Solutions of Tartaric and Racemic Acids . 964
Mulder (E.). Tartrotartaric Acid 965
Lederer (L.). Amido- and Methamido-crotonanilide 965
Probst (O.). Derivatives of Thiocarbamide and Carbamide . . . 966
Sachs (H.). Thiophenchlorophosphine and its Derivatives 966
Maquenne. Action of Sulphuric Acid on Hydrocarbons with a Closed Chain 967
Töhl (A.). Halogen Derivatives of Methylbenzenes 967
Töhl (A.). Action of Sulphuric Acid on Bromoprehnitene 968
Töhl (A.). Action of Sulphuric Acid on Chlorodurene 968
Töhl (A.) and A. Geyger. Symmetrical and Unsymmetrical Ethylmetaxylene 968
Schall (C.). Sodium Phenyl Sulphide 970
Zincke (T.). Action of Bleaching Powder and of Hypochlorous Acid on Quinones 970
Meyer (R.) and H. Hoffmeyer. Fluoresceïn 970
Hollemann (A. F.). Dinitrosacyls 971
Ciamician (G.) and P. Silber. The Oxymethylene Group in Isosafrole . 972
Limpricht (H.) and F. Meyer. Azobenzene-, Hydrazobenzene-, and Benzidine-disulphonamides 973
Goldschmidt (H.) and A. Pollak. Hydroxyazo-compounds 974
Goldschmidt (H.) and B. Bardach. Diazoamido-compounds 977
De Vries (H. J. F.) and A. F. Hollemann. Phenylhydrazine Acetate . 981
Bölsing (F.) and J. Tafel. Acid Hydrazides 981
Pinner (A.). Mixed Acid Amides 982
Freund (M.) and H. Wolf. Action of Thiocarbonyl Chloride on Aromatic Thiocarbamides 983
Holle (O.). Tertiary Phosphines and Arsines 984
Hollemann (A. F.). Isonitrosoanilacetone. 985
Claus (A.). Aromatic Alkyl Ketones and their Oximes 985
Fittig (R.) and R. Ruer. Oxidation of Cinnamic Acid 986
Fittig (R.) and P. Obermüller. Oxidation of Phenylisocrotonic Acid . 986
Fittig (R.) and E. Mayer. Oxidation of Hydrocinnamenylacrylic Acid . 986
Fittig (R.) and P. Obermüller, and C. Schiffer. Decomposition of Phenyldibromobutyric Acid 987
Fittig (R.) and J. Stern. Decomposition of Phenyldibromovaleric Acid . 987
Fittig (R.) and J. Stern. Hydrocinnamenylacrylic Acid 988
Fittig (R.) and R. Claus. New Derivatives of Coumarin 988
Goldschmiedt (G.) and R. Jahoda. Ellagic Acid 990
Töhl (A.) and D. v. Karchowski. Ethylpseudocumene and the Action of Sulphuric Acid on it 990
Otto (R.) and E. Heydecke. Aromatic Thiosulphonates 990
O'Neill (C.). Products from Indigo-Blue 991
Soxhlet (V. H.). Indigo-Green 991
Cathcart (W. R.) and V. Meyer. Formation of Closed Chain Compounds by the Elimination of Bromine from the Benzene Nucleus . . . 992
Delacre (M.). Synthesis of Symmetrical Triphenylbenzene . . . 993
Klingemann (F.). Action of Phenylhydrazine on Unsaturated γ-Diketones 995

PAGE

Reverdin (F.) and C. de la Harpe. Amidonaphtholsulphonic Acids . 996
Wallach (O.) and G. Lorentz. Pinylamine 996
Wallach (O.). Constitution of Pinene 997
Wallach (O.) and E. Früstück. Nitrolamines of Pinene. . . . 997
Wallach (C.) and E. Früstück. Preparation of Pinole Glycol and its Derivatives 998
Wallach (O.) and A. Berkenheim. Tetrahydropinene 998
Cazeneuve (P.). Nitroketone from Camphosulphophenols 999
Spiegel (L.). Action of Phenylhydrazine on Cantharidin 999
Christensen (O. T.). Compounds of Hydrogen Diaminechromium Thiocyanate with Nitrogenous Bases 1000
Rügheimer (L.). The Compound $C_{36}H_{28}N_4O_6$ obtained by the Action of Sodium Ethoxide on Ethyl Hippurate 1002
Klingemann (F.). Desylacetic Acid 1002
Murmann (E.). Derivatives of α-Phenylquinoline 1003
Lederer (L.). Nomenclature of Pyrazolones 1004
Michaelis (A.) and R. Burmeister. Ethyl Malonate Phenylhydrazide and 1-Phenyl-3 : 5-pyrazolidone 1004
Pinner (A.). Furfuran Compounds 1006
Bladin (J. A.). Tetrazole 1009
Pinner (A.) and R. Wolffenstein. Nicotine 1010
Hesse (O.). Conversion of Cupreïne into Quinine 1010
Comstock (W. J.) and W. Koenigs. Halogen Derivatives of the Cinchona Alkaloïds 1010
Claus (A.). Alkyl Derivatives of Cinchona Alkaloïds. 1012
Tafel (J.). Strychnine 1012
Einhorn (A.) and L. Fischer. Nitroatropine 1014
Einhorn (A.) and L. Fischer. Action of Hypochlorous Acid on Tropine. 1014
Einhorn (A.) and B. Rassow. Dihydroxyanhydroecgonine . . . 1015
Griffiths (A. B.). Pinnaglobin, a New Globulin 1016
Böttinger (C.). Peptone Salts of Glutin 1016
Bohr (C.) and S. Torup. Oxygen in Oxyhæmoglobin Crystals . . . 1017
Bertin Sans (H.) and J. Moitessier. Formation of Oxyhæmoglobin from Hæmatin and a Proteïd 1017
Keppler (F.) and V. Meyer. 1 : 3-Dinitropane 1061
Askenasy (P.) and V. Meyer. Nitropropylene 1062
Béhal (A.) and A. Desgrez. Action of Organic Acids on Acetylenic Hydrocarbons 1064
Maquenne (L.). Hydrocarbon derived from Perseïtol. 1065
Fleurent (E.). Action of Potassium Cyanide on Ammoniacal Cupric Chloride 1065
De Forcrand. Sodiotrimethylcarbinol: Value of the Tertiary Alcoholic Function 1066
Ullik (F.). Carbohydrates. 1066
Kirpal (A.). First Product of the Reduction of Nitro-compounds with Stannous Chloride 1067
Schiff (R.). Special Case of Isomerism 1067
Kremers (E.). Citronellic Aldehyde 1068
Meslans (M.). Acetic Fluoride 1068, 1069
Hantzsch (A.). Configuration of the Aldoximeacetic Acids or β-Oximidopropionic Acids 1069
Claisen (L.). Action of Ethyl Chlorocarbonate on Ethyl Sodacetoacetate . 1070
Guareschi (I.). Action of Ethyl Cyanacetate on Organic Bases. . . 1071
Quenda (E.). Action of Ethyl Cyanacetate on Aniline 1072
Claisen (L.). Constitution of Ethyl Acetoacetate, and of the so-called Formyl Derivatives of Ethereal Salts and Ketones. 1072
Thal (K.). Action of Nitrous Acid on Ethyl Acetosuccinate and Diacetosuccinate 1074
Stohmann (F.) and C. Kleber. Hydrogenation of Closed Rings . . 1074
Baeyer (A.). Synthesis of Dihydrobenzene 1074

PAGE
Heusler (F.). Lignite Tar 1075
Schall (C.) and J. Uhl. Action of Iodoform on the Additive Product obtained from Sulphurous Anhydride and Sodium Phenoxide . . 1076
Kehrmann (F.). Thymol 1078
Causse (H.). Orthophenylene Hydrogen Antimonite 1078
Weinberg (A.). Paramidoalkylorthotoluidines 1078
Lang (W.). Oxalylorthamidophenyl Mercaptan and Oxalylorthamido-α-naphthyl Mercaptan 1079
Willgerodt (C.). Dinitrosoazobenzene 1079
Mai (J.). Action of Diazo-compounds on Oximes 1079
Claus (A.). Oximes 1080
Stolz (F.). Parethoxyphenylhydrazine and Dimethylparethoxyphenylpyrazolone 1080
Altschul (J.). Paralkyloxy-derivatives of Phenylhydrazine, Hydracetine, and Antipyrine 1080
Hantzsch (A.). Isomeric Oximes and Hydrazones 1083
Hammerich (H.). Derivatives of Dibenzylcarbamic, Paraditolylcarbamic, and Benzylparatolylcarbamic Acids 1083
Hammerich (H.). Tetrabenzyloxamide and Tetraparatolyloxamide . . 1084
Hammerich (H.). Action of Silver Cyanide on Dibenzylchlorocarbamide and Paraditolylchlorocarbamide 1084
Michaelis (A.) and F. Rothe. Aromatic Phosphorus Compounds . . 1084
Cazeneuve (P.). Ethylnitroketone and Acetylnitroketone from Camphosulphophenols 1085
Graebe (C.) and K. Lagodzinski. Phenylanthranilic Acid and Acridone 1086
Carrick (J. T.). Condensation of Ethyl Cyanacetate and Benzaldehyde: Ethyl α-Cyanocinnamate 1086
Michaël (H. A.) and J. Jeanprêtre. Mandelic Acid and its Nitrile . 1088
Lagai (G.). Ethoxyphenylsulphonic Acids 1089
König (G.). Oxidation Products of Mercapturic Acids 1090
Weber (O.). Toluic Sulphinide (Methylsaccharin) 1092
Lauth (C.). Diamidosulphobenzide and its Derivatives 1093
Noyes (W. A.). Dibenzylcarbinamine 1093
Michaël (H. A.) and J. Jeanprêtre. Formation of Aromatic Nitriles . 1094
Bernthsen (A.). Ammonium Bases of Phenylacridine 1095
Trillat (A.) and De Raczkowski. Azo- and Alkyl Compounds of Chrysaniline and the Colouring Matters derived therefrom . . . 1095
Wachter (W.). Desaurin 1095
Grande (E.). Phenolphthaleïn Ethyl Ether 1096
Kostanecki (S. v.) and R. Rutishauser. Hydroxyanthones . . . 1096
Kostanecki (S. v.) and S. Seidmann. Bye-products in the Preparation of Hydroxyanthones 1097
Heermann (P.). 1 : 4-Amidonaphthol Ethyl Ether and its Derivatives . 1097
Kowalski (M.). Hydroxyquinones 1098
Kostanecki (S. v.). Xanthones and Hydroxyxanthones of the Naphthalene and Quinoline Series 1098
Bener (P.). Xanthones and Hydroxyxanthones of the Naphthalene Series 1099
Donner (A.). Benzeneazo-α-naphthylglycocine 1100
Brühl (J. W.). Terpenes and their Derivatives 1100
Stohmann (F.) and C. Kleber. Constitution of Camphoric Acid . . 1103
Shamel (C. H.). Eupatorin 1103
Denigès (G.). Action of Pyridine Bases on Sulphites 1103
Tafel (J.). Oxidation of Reduced Pyridine and Quinoline Bases . . 1104
Vis (G. N.). 1 : 4-Ethoxyacetamidoquinoline 1104
Brühl (J. W.). Action of Sodium and Carbonic Anhydride on Antipyrine 1106
Eliasberg (J.) and P. Friedländer. Condensation of Orthamidobenzaldehyde 1106

PAGE

KEHRMANN (F.) and J. MESSINGER. Azonium Compounds . . . 1108
HOFMANN (A. W. v.) and S. GABRIEL. Action of Iodine on Thiobenzamide 1109
PINNER (A.). So-called Dibenzimidine 1110
CIAMICIAN (G.) and P. SILBER. Pseudopelletierine 1110
BRENZINGER (K.). Cystin and Cysteïn 1111
VIGNON (L.) and P. SISLEY. Nitrated Silk 1111
BÉHAL and DESGREZ. Action of Fatty Oils on Olefines 1162
ERÜHL (J. W.). Trimethylene 1163
KRAFFT (F.) and L. REUTER. Higher Homologues of Acetylene. . . 1163
GUENEZ (E.). Arsenic Cyanide 1164
AUFSCHLÄGER (H.). Formation of Zinc Cyanide on Heating Nitrogenous Organic Substances with Zinc-dust. 1164
FISCHER (E.) and Others. Sugars Richer in Carbon from Glucose . . 1164
SCHULZE (E.). β-Galactan 1171
ROUVIER (G.). Iodide of Starch 1171
PETIT (P.). Product of the Oxidation of Starch 1171
BERG (A.). Chlorinated Derivatives of Isobutylamines 1172
HARTUNG (L.). Hexamethylenamine 1173
DOLLFUS (W.). Configuration of Aldoximes 1174
HANTZSCH (A.). Relations between Constitution, Configuration, and Chemical Behaviour of Oximes 1175
NUSSBERGER (G.). Stereoisomeric Dioximes from Ethyl Acetoacetate and Benzoyl Acetate 1175
KUBEL. Action of Magnesium Acetate on Magnesium Oxide and on Lead Oxide 1178
MICHAEL (A.). Constitution of Ethyl Sodacetoacetate 1178
ANGELI (A.) and A. CHIUSSI. Action of Iodic Acid on Levulinic Acid . 1179
SCHEIBLER (C.) and H. MITTELMEIER. So-called Isoarabonic Acid . . 1180
PHOOKAN (R. D.) and F. KRAFFT. Derivatives of Sebacic Acid . . . 1180
ANSCHÜTZ (R.) and E. PARLATO. Ethyl Dioxosuccinate 1181
MULLER (P. T.). Action of Ethyl Salts of Unsaturated Acids on Ethyl Sodiocyanacetate 1181
MARKOVNIKOFF (V.). Naphthenes and their Derivatives in the General System of Organic Compounds. 1182
JACKSON (C. L.) and W. B. BENTLEY. Tribromonitrobenzene . . . 1182
BAEYER (A. v.). Synthesis of Dihydroparaxylene 1182
EITNER (P.) and F. KRAFFT. Mechanism of the Formation of Tricyanides from Nitriles and Acid Chlorides in Presence of Aluminium Chloride . 1183
DE FORCRAND. Monosodium Catechol 1184
DE FORCRAND. Sodium Resorcinol and Sodium Quinol 1184
DE FORCRAND. Dimetallic Derivatives of Dihydric Phenols . . . 1185
ZINCKE (T.). Action of Chlorine on Phenols 1186
VAUBEL (W.). Phenylene Oxide 1187
ULRICH (B. C.). Oxidation of Bisecondary Pentethylphloroglucinol by means of Uncombined Oxygen 1188
HEIDENREICH (A.) and V. MEYER. Formation of Diphenylamine from Orthobromobenzoic Acid. 1188
MILLER (W. v.), J. PLÖCHL, and Others. Schiff's Bases 1889
BISTRZYCKI (A.) and F. ULFFERS. Diacetylorthodiamines 1197
PALMER (A. W.). Reduction of Symmetrical Triamidonitrobenzene . . 1198
KEHRMANN (F.). Dinitrosoazobenzene 1198
HIRSCH (R.). New Synthesis by means of Diazo-compounds . . . 1198
ALTSCHUL (J.). Parahydroxyalkyl Derivatives of Phenylhydrazine . . 1198
ANGELI (A.). Action of Nitrous Acid on certain Unsaturated Aromatic Compounds 1198
BEHREND (R.) and D. NISSEN. Orthochlorobenzaldoximes. . . . 1199
CLAUS (A.). Aromatic Alkyl Ketoximes 1200
DOLLFUS (W.). Configuration of γ-Ketoximic Acids 1202
SCHIFF (H.). Amidotolylurethane 1203

PAGE

PULVERMACHER (G.). Mandelamide 1203
HALLER (A.). Modes of Formation of Substituted Imides 1204
LOUISE (E.) and PERRIER. Metallic Compounds of Aromatic Ketones . 1205
CLAUS (A.) and A. WEIL. Dibromobenzoic Acids 1205
CLAUS (A.) and A. STAVENHAGEN. Dichlorobenzoic Acids 1206
CLAUS (A.) and L. BECK. Nitration and Bromination of Parabromortho-toluic Acid 1207
SCHIFF (H.) and A. VANNI. Amido- and Urethano-tolyloxamic Acid. . 1208
GRAEBE (C.) and A. EICHENGRÜN. Action of Heat on Salicylic Acid . . 1208
WEGSCHEIDER (H.). Methyl Salts of Abnormal Structure . . . 1208
TUST (K.). Bromopianic Acid 1209
MILLER (W. v.) and G. ROHDE. α-Phenylhydrocinnamic Acid . . . 1211
BAEYER (A. v.). Reduction Products of Phthalic Acid. Constitution of Benzene 1211
JACKSON (C. L.) and W. B. BENTLEY. Products of the Action of Nitric Acid on Ethyl Bromotrinitrophenylmalonate 1217
KRAFFT (F.) and A. ROOS. Alkyl Salts of Sulphonic Acids. . . . 1219
MILLER (W. v.) and G. ROHDE. Phenylhydrindone 1220
YOUNG. Condensation of the three Isomeric Methylhydrocinnamic Acids to the corresponding Methylhydrindones 1221
MIERSCH (W.). Formation of Hydrindone Derivatives from Halogen-cinnamic Acids 1222
LAUTH (C.). Metadiamidotetramethylbenzidine 1222
SCHIFF (H.). Polymethylene Bases from Benzidine and Tolidine . . 1223
SCHÖPFF (M.). Acridone Derivatives 1223
SUDBOROUGH (J. J.). Isomeric Change in the Stilbene Series . . . 1224
GRAEBE (C.) and A. EICHENGRÜN Hydroxyketone Dyes 1224
GRAEBE (C.) and A. EICHENGRÜN. Behaviour of Aromatic Hydroxy-ketones with Sulphuric Acid and with Ammonia 1226
PETRENKO-KRITSCHENKO (P.). Derivatives of Deoxybenzoïn . . . 1227
MEYER (R.) and H. HOFFMEYER. The Fluoresceïn Group 1228
LIEBERMANN (C.) and A. HARTMANN. Condensation of Cinnamic Acid with Hydrocarbons. 1228
GAESS (F.). Nitro-β-naphthol 1229
ZINCKE (T.). Nitro-β-naphthaquinone. 1229
ZINCKE (T.) and M. LATTEN. Action of Chlorine on Nitro-β-naphthaquinone in Glacial Acetic Acid Solution. 1229
ZINCKE (T.) and O. SCHARFENBERG. Action of Chlorine on Nitro-β-naphthaquinone in Chloroform Solution 1232
FRIEDLÄNDER (P.) and S. SZYMANSKI. Nitration of β-Naphthylamine . 1232
MAQUENNE. Natural Synthesis of the Vegetable Hydrocarbons . . 1234
MERCK (E.). Terpin Hydrate from Eucalyptus Oil 1235
BERTRAM (J.) and H. WALBAUM. Oil of Lavender and of Bergamot . . 1235
BARBIER (P.). Essential Oil of Licari Kanali 1236
WALLACH (O.). Camphor and Fenchone Series 1236
WALLACH (O.) and J. GRIEPENKERL. Comparison of Bornylamine and Fenchylamine. 1238
WALLACH (O.) and L. JENCKEL. Fencholamine 1240
BRÜHL (J. W.). Camphene and Camphoric Acid 1240
SENGER (O.). Absinthin from *Artemisia absinthum* 1240
BECKURTS (H.). Anemonin 1241
KILIANI (H.). Digitalonic Acid 1241
GAUTIER (A.). Origin of the Colouring Matters of the Vine: Ampelochroïc Acid 1242
LIPP (A.). Synthesis of Tetrahydropyridine Derivatives, and their Conversion into Piperidine Derivatives 1243
LIPP (A.). 1-Methyl-Δ^2-tetrahydro-2-hydroxyethylpyridine. . . . 1244
MILLER (W. v.). Synthesis of Quinaldine 1245
MÖLLENHOFF (O.). Methylphenylpyrazolone and its Derivatives. . . 1245
WITT (O. N.) and C. SCHMIDT. Azonium Bases 1246

PAGE

Forssel (G.). Action of Ethylenediamine on Thiamides 1247
Bistrzycki (A.) and G. Cybulski. Phthalamidones 1248
Claus (A.). Cinchona Alkaloïds 1249
Grimaux (E.) and A. Arnaud. Bases Homolgous with Quinine . . 1253
Jungfleisch (E.) and E. Leger. Apocinchonine and Diapocinchonine . 1253
Ehrenberg (A.) and C. Purfurst. Aconitine 1254
Schmidt (E.). Scopolamine (Hyoscine) 1255
Merck (E.). Subsidiary Alkaloïds of Belladonna 1255
Griffiths (A B.). Chlorocruorine 1256
Menschutkin (N.) and M. Vasileff. Affinity Coefficients of Alkyl Iodides and Bromides 1289
Kisel (I.). Action of Methyl Iodide and of Chloroform on Nitroisopropane 1290
Tscherven-Iwanoff. Polymerides of Dichloracetonitrile and Trichloracetonitrile 1291
Moissan (H.). Carbon Diiodide 1291
Brochet (A.). Action of Chlorine on Isobutyl Alcohol 1292
Demyanoff (N.). Pentamethylene Glycol and its Oxides 1292
Gustavson (G.). Action of Zinc dust and Alcohol on Chlor-α-dibromhydrin 1293
Istrati and Edeleanu. Action of Acetic Anhydride on Glucose . . 1293
Baufr (R. W.). Sugar from Linseed 1293
Lintner (C. J.). Isomaltose 1293
Koydl (T.). Precipitation of Raffinose by Ammoniacal Lead Acetate. . 1294
Gérard. Vegetable Cholesterol 1294
Malbot (H.) and A. Malbot. Action of Propyl Iodide on Trimethylamine. Trimethylpropylammonium Iodide. 1294
Malbot (H.) and A. Malbot. Action of Isopropyl Iodide on Trimethylamine. Trimethylisopropylammonium Iodide 1295
Malbot (H.) and A. Malbot. Action of Allyl Iodide on Trimethylamine. Trimethylallylammonium Iodide 1295
Thiele (J.). Nitroguanidine and Amidoguanidine 1295
Duclaux. Supposed Reaction of Spermine. 1300
Reformatsky (S.). Action of Zinc and Ethyl Monochloracetate on the Aldehydes 1300
Simonini (A.). Action of Iodine on the Silver Salts of Fatty Acids . . 1301
Zelinsky (N.) and A. Buitchichin. An Additive Compound of Hydrogen Cyanide with Ethyl α-Cyanopropionate 1301
Duvillier (E.). Dimethylamidopropionic Acid 1302
Duvillier (E.) and F. Chancel. Action of Ammonia on Bromisobutyric Acid 1302
Marie (T.). Monobromocerotic Acid 1302
Henry (P.). Reciprocal Transformation of Lactones and Hydroxy-acids . 1303
Mangold (K.). Stereochemistry of Trihydroxystearic Acids prepared from Ricinoleïc Acid and from Ricinelaïdic Acid 1304
Kondakoff (I.). Constitution of Tiglic and Angelic Acids. . . . 1304
Tanatar (S.). Action of Methylene Iodide on Diethyl Malonate . . 1304
Tanatar (S.). Action of Alcoholic Potash on Bromisosuccinic Acid . . 1305
Tanatar (S.). Transformation of Maleïc and Fumaric Acids . . . 1305
Tanatar (S.). Complete Transformation of Fumaric into Maleïc Acid . 1306
Markovnikoff (V.). Tetramethylenedicarboxylic Acids 1306
Kanonnikoff (A. A.). Specific Rotatory Power of Tartaric Acid and its Salts 1308
Bourgeois (L.). Volatility of Carbamide and its Crystallisation by Sublimation in a Vacuum 1309
Carrara (G.). Thiourea 1309
Heise (P.) and A. Töhl. Action of Aluminium Chloride on Aromatic Hydrocarbons. 1309
Reuter (L.). Synthesis of Cymene 1310
Lazareff (P.). Displacement of Hydrogen by Haloïds in Aromatic Hydrocarbons 1310

PAGE
ISTRATI and GEORGESCU. Iodobenzenes 1310
MARKOVNIKOFF (V.). Naphthenes and Polymethylenes 1310
MARKOVNIKOFF (V.). Naphthenes and their Derivatives in the General System of Organic Compounds 1311
VIDAL (R.). Action of Non-metallic Nitrides and Hydronitrides on Hydroxy-carbon Compounds 1311
BAYRAC (P. H.). Indothymol and Thymoquinone 1311
REYCHLER (A.). Preparation of Carvacrol 1311
REYCHLER (A.). Some Derivatives of Carvacrol 1312
BÉHAL and DESVIGNES. "Asbolin" 1312
CAUSSE (H.). Acetoneresorcinol 1312
DE FORCRAND. Sodium Pyrogallol 1313
CAZENEUVE (P.). Conversion of Gallic Acid into Pyrogallol . . . 1314
BARTOLOTTI (P.). Action of Phosphorus Pentachloride on Methylhydroco-toïn and Methylprotocotoïn 1314
BARTOLOTTI (P.). Derivatives of Isoapiole 1315
CHABRIÉ (C.). Organic Halogen and Boron Derivatives 1316
TASSINARI (G.). Constitution of Dihydroxythiobenzenes 1316
SPRING (W.) and J. VAN MARSENILLE. Thiopinacone 1317
MARCHESINI (G.). Carbaminethioacetophenone 1317
ALEXANDER (H.). Reduction of Coumarone 1318
HERZIG (J.). Fluorescin, Galleïn, and Aurin 1319
ROSENSTIEHL (J.). Influence of Nucleal Methyl on the Properties of Ortho-toluidine 1319
ALEXANDER (H.). Action of Formaldehyde on Orthodimethyltoluidine . 1320
JABLIN-GONNET. Action of Benzyl Chloride on Unsymmetrical Meta-xylidine 1320
MICHAELIS (A.) and J. RABINERSON. Action of Arsenious Chloride on Tertiary Aromatic Amines 1321
WILLGERODT (C.). Constitution of Nitrosoazo-compounds 1321
STRACHE (H.) and M. KITT. Oxidation of Phenylhydrazine with Fehling's Solution 1322
PELIZZARI and D. TIVOLI. Action of Cyanogen Chloride on Phenyl-hydrazine 1323
EDELEANU (L.). Action of Phenylhydrazine on Carbamide 1323
MICHAELIS (A.). Inorganic Derivatives of Phenylhydrazine . . . 1324
MICHAELIS (A.) and J. RUHL. Thionyl Chloride and Aromatic Hydr-azines 1324
MICHAELIS (A.) and F. OSTER. Action of the Chlorides of Phosphorus, Arsenic, Boron, and Silicon on Aromatic Hydrazines 1324
RUHL (J.). Parathiophenylhydrazine and Thionylthioaniline . . . 1326
MARCKWALD (W.). Imidazoles and the Constitution of Glyoxaline . . 1326
GABRIEL (S.) and A. NEUMANN. Formation of Oxazolines 1331
CAZENEUVE (P.). Instability of Carboxyl in Phenolic Acids . . . 1332
PRATESI (L.). Orthoparadinitrophenylglycollic Acid 1333
BISCHOFF (C. A.) and A. HAUSDÖRFER. Derivatives of Phenylglycocine and Orthotolylglycocine 1333
BISCHOFF (C. A.) and A. HAUSDÖRFER. Paratolylglycocine and its Derivatives 1335
BISCHOFF (C. A.) and A. HAUSDÖRFER. Derivatives of α-Amidopropionic Acid 1336
BISCHOFF (C. A.) and N. MINTZ. Derivatives of α-Amidobutyric Acid . 1338
BISCHOFF (C. A.) and N. MINTZ. Anilidoisobutyric Acids 1338
BISCHOFF (C. A.) and N. MINTZ. Toluidoisobutyric Acids 1339
FIQUET (E.). Synthesis of Unsaturated Nitriles 1340
PFANNENSTILL (E.). Xylenedisulphonic Acids 1340
GAESS (F.). Nitro-β-naphthols 1341
BISCHOFF (C. A.) and A. HAUSDÖRFER. Derivatives of Naphthylglycocines 1341
BISCHOFF (C. A.) and N. MINTZ. Derivatives of α- and β-Naphthylidoiso-butyric Acids, &c. 1342

PAGE

Alvisi (U.). The Camphor Group 1343
Minguin (J.). Methyl Camphocarboxylates, Methylcamphor, and Azo-derivatives of Cyanocamphor 1343
Haller (A.). Alkylcyanocamphors and Alkylbenzeneazocamphocarboxylates 1344
Errera (G.). Action of Potassium Hypobromite on the Amide of Campholic Acid 1345
Haller (A.). Function of Camphoric Acid. 1346
Haller (A.). Constitution of Camphoric Acid 1347
Schimmel. Essential Oils 1347
Wallach (O.). Isomerism in the Limonene Series 1348
Reychler (A.). Constitution of Carvene 1350
Wallach (O.) and A. Hesse. Action of Chlorine on Dihydrochlorodipentene 1350
Shtchoukareff (A.). Degree of Saturation of the Dextroterpene from Russian Turpentine 1350
Shtchoukareff (A.). Reduction of Hydrate of Terpinol 1351
Carrara (G.). Condurangin 1352
Francesconi (L.). Santonic Acid 1352
Grandis (V.). Chrysophanic Acid 1354
Herzig (J.). Euxanthic Acid and Euxanthone 1354
Monteverde (N.). Chlorophyll 1355
Pictet (A.) and G. Krafft. Chloriodides of Organic Bases . . . 1356
Zaloziecki (R.). Pyridine-like Bases in Petroleum 1357
Mayer (R.). Pyridinecarboxylic Acids obtained from Berberine . . 1357
Prausnitz (G.). Derivatives of 2-Methyl-5-ethylpyridylalkine . . . 1358
Claus (A.). Quaternary Ammonium Bases of the Quinoline Series . . 1358
Hinsberg (O.). Methylhydroxytoluquinoxaline and the Constitution of the Compounds obtained from α-Hydroxy-acids and Orthodiamines . . 1359
Schuster (F.). Action of Benzaldehyde on 2 : 6-Lutidine 1360
Heiber (F.). Diethyl Hydrofurfuryllutidinedicarboxylate and its Derivatives 1362
Peratoner (A.). Sparteïne 1362
Grimaux (E.). Quinine Methiodides 1363
Lippmann (E.) and F. Fleissner. The Hydriodo-compounds of the Cinchona Alkaloïds 1363
Rügheimer (L.). Condensation of Aldehydes with Benzoylpiperidine . 1364
Blau (F.). αβ-Dipiperidyl 1365
Ladenburg (A.). Hyoscine 1366
Freund (M.) and W. Josephy. Alkaloïds of the root of *Corydalis cava* . 1366
Griffiths (A. B.). A New Leucomaïne 1367
Meyer (V.) and F. Müller. Substitution in the Aliphatic Series . . 1414
Keppler (F.). and V. Meyer. 1 : 3-Dinitropropane 1415
Russanow (A.). Action of Silver Nitrite on Methylene Iodide . . . 1415
Keiser (E. H.). Silver and Copper Compounds of Acetylene . . . 1416
Vitali (D.). Action of Hydrogen Cyanide on Mercurous Salts . . . 1416
Seidel (P.). Fulminuric and Deoxyfulminuric Acids 1417
Tcherniac (J.). Water of Crystallisation of Barium Thiocyanate . . 1418
Purgotti (A.). New Thiosulphates 1418
Crossley (A. W.). Optical Properties of Dulcitol and its Derivatives . 1419
Schulze (C.) and B. Tollens. Disappearance of the Multirotation of Sugars in Ammoniacal Solution 1419
Schulze (C.) and B. Tollens. Xylose and its Optical Properties . . 1420
Schulze (C.) and B. Tollens. The Pentosans of Woody Vegetable Fibre. 1420
Schnelle (W.) and B. Tollens. Multirotation of Rhamnose and the Saccharins 1420
Isaac (J. F. V.). Production of Acetic Acid from Cellulose and other Carbohydrates. Lignocellulose and Ferric Ferricyanide . . . 1421
Kirkaldy (P. H.). Urea Oxalate 1421
Chancel (F.). Propylcarbamide and Unsymmetrical Dipropylcarbamide . 1421

PAGE

Carrara (G.). Preparation of Methylethylsulphine and Methyl Ethyl Sulphide 1422
Hofmann (A. W. v.) and F. Mahla. Diethyldithiophosphinic Acid . . 1422
Kekulé (A.). Formaldehyde 1423
Orndorff (W. R.) and S. B. Newbury. Preparation of Aldol and Crotonaldehyde. 1423
Lieben (A.). Preparation of Crotonaldehyde 1424
Fischer (E.) and K. Landsteiner. Glycolaldehyde 1424
Tcherniac (J.). Chloracetone 1425
Tcherniac (J.). Thiocyanacetone 1425
Tcherniac (J.). Preparation and Estimation of Thiocyanacetone . . 1426
Holt (A.). Stereometric Relation of Erucic and Brassidic Acids . . 1427
Michael (A.). Constitution of Ethyl Sodacetoacetate 1428
Magnanini (G.) and M. Scheidt. Action of Phenylhydrazine and Hydroxylamine on Dehydrodiacetyllevulinic Acid 1429
Thiele (J.). Azodicarboxylic Acid 1429
Seubert (K.) and G. Rauter. Copper Oxalate and Cuprammonium Oxalate 1431
Wislicenus (W.). Inactive Ethyl Malate 1431
Schnelle (W.) and B. Tollens. Polarisation Phenomena of Rhamnonic Acid and Rhamnolactone 1431
Schnelle (W.) and B. Tollens. Polarisation Phenomena of Gluconic Acid and Gluconolactone 1432
Schnelle (W.) and B. Tollens. Polarisation Phenomena of Galactonic Acid and Galactonolactone 1432
Conrad (M.). Isarabic Acid 1432
De Lisle (A.). Thetincarboxylic Acids 1433
Günther (A.), G. de Chalmot, and B. Tollens. Formation of Furfuraldehyde from Glycuronic Acid Derivatives and from Albumin . . 1433
Goldschmidt (H.) and E. Zanoli. Hydroximes of Furfuraldehyde, Thiophenaldehyde and Œnanthaldehyde 1433
Brühl (J. W.). Dipropargyl and Benzene 1436
Haeussermann (C.) and C. Beck. Action of Chlorine on Orthonitrotoluene in presence of Sulphur 1437
Ahrens (C.). Derivatives of Metaxylene 1437
Nef (J. U.). Bivalent Carbon 1438
Cousin (H.). Homocatechol and Two Nitrohomocatechols . . . 1443
Koenigs (W.) and C. Mai. Condensation of Unsaturated Hydrocarbons with Phenols 1443
De Forcrand. Constitution of Pyrogallol 1446
Fischer (E.) and A. J. Stewart. Aromatic Sugars 1447
Pesci (L.). Mercurioanilido-compounds 1448
Biltz (H.). Additive Products of Hydrogen Iodide and Nitriles . . 1449
Pulvermacher (G.). Condensation Products with Formaldehyde . . 1450
Brunck (O.). Derivatives of Paradianilidobenzene 1450
Haegele (E.). Condensation Products of Amidophenols 1451
De Chalmot (G. J. L.). Condensation Products of Furfuraldehyde with Bases 1451, 1452
Schall (C.) and S. Paschkowetzky. Stereoisomerism of Carbodiphenylimide and Carboparaditolylimide 1452
Willgerodt (C.). Constitution of Nitrosoazo-compounds 1453
Martina (G.). Metallic Derivatives of Phenylhydrazine 1454
Paal (C.) and A. Bodewig. Action of Orthonitrobenzyl Chloride on Phenylhydrazine 1455
Reissert (A.). α-Phenylhydrazidopropionic Acid 1456
Behrend (R.) and E. König. Alkyl Derivatives of Hydroxylamine . . 1456
Bridge (J. L.). Quinoneoxime Ethers 1456
Hinsberg (O.). Action of Amido-bases on Sodium Glyoxalsulphonate . 1458
Bradley (W. P.) and F. B. Dains. Action of Acetic Chloride on Orthohydroxyaldehydes 1458

PAGE

Lange (K.) and A. Zufall. Preparation of Aromatic Nitro-ketones . . 1459
Meyer (V.) and W. Wachter. Iodosobenzoic Acid 1460
Zincke (T.) and O. Fuchs. Hexachlorometadiketohexene. Action of Chlorine on 1 : 3 : 5-Dihydroxybenzoic Acid 1461
Nissen (C.). αβ-Dichlorocinnamic Acid 1464
Lowenherz (R.). Asymmetrical Amidoisophthalic Acid 1464
Töhl (A.). Chlorodurenesulphonic Acid 1465
Bischler (A.). Formation of Substituted Indoles 1465
Pulvermacher (G.) and W. Loeb. Carbazole 1466
Helle (J.). Orthotolidinedisulphonic Acid 1466
Caro (N.). Hydroxyaurin and Hydroxyaurincarboxylic Acids . . . 1469
Täuber (E.) and E. Halberstadt. Synthesis of Diphenylene Oxide . 1470
Siegfeld (M.). Action of Aniline on Benzile 1470
Auwers (K.) and M. Siegfeld. Benzileoximes 1470
Carlson (M.). Acids from the Dicyanhydrin of Benzoylacetone. . . 1471
Braun (L.) and R. Ebert. Naphthalene Dihydrosulphide and Dithiocyanate 1471
Fischer (O.). Orthodiamines 1472
Fischer (O.) and E. Hepp. Formation of Indulines 1476
Schöpff (M.). Action of Aniline on β-Naphtholcarboxylic Acid . . 1476
Cleve (P. T.). 1 : 2-Dicyanonaphthalene and 1 : 2-Naphthalenedicarboxylic Acid 1477
Cleve (P. T.). Chloronaphthalenesulphonic Acids 1477
Cleve (P. T.). 1 : 2 : 2′-α-Nitrochloronaphthalenesulphonic Acid . . 1478
Reissert (A.) and A. Junghahn. 3′-Methyl-α-naphthindole . . . 1479
Sieker (F. A.) and E. Kremers. Menthene 1479
Piccard (J.). Cantharene 1480
Elkeles (G.). Cineolic Acid 1480
Kwasnik (W.). Kuromoji Oil 1480
Wallach (O.). Camphene and Camphoric Acid 1481
Chaplin (E. M.). Hydrazones of Camphoric Acid 1481
Tilden (W. A.). Spontaneous Conversion of Isoprene into Caoutchouc . 1482
Kiliani (H.). Digitalin 1482
Kiliani (H.). Preparation of Digitogenin 1483
Leprince. Cascarin 1483
Karau (G.). Tetravinylpyridine 1483
Varet (R.). Piperidine Compounds 1483
Wolffenstein (R.). Oxidation of Piperidine by Hydrogen Peroxide. . 1484
Ladenburg (A.). Nipecotinic Acid 1485
Ladenburg (A.) and G. Karau. Isonipecotinic Acid. 1486
Ladenburg (A.). Piperidinecarboxylic Acids 1486
Kirchner (L.). Phenyllutidinedicarboxylic Acid and Phenyllupetidinedicarboxylic Acid 1486
Ladenburg (A.). Dimethyldipiperidyl 1487
Berend (L.) and E. Thomas. Ketones of the Quinoline Series . . . 1488
Ephraim (J.). Amidoquinolines 1488
Claus (A.). Alkyl and Alkylene Derivatives of Cinchonic Acid and Alkylene Derivatives of Cinchoxinic Acid 1488
Pinkus (G.). Action of Trimethylene Chlorobromide on Aromatic Amines and Amides 1491
Hesse (O.). Cincholine and Fluoroline 1492
Rung (F.) and M. Behrend. Glyoxaline 1493
Busch (M.) and M. Klett. Cinnoline Derivatives 1494
Michaelis (A.) and R. Hermens. β-Succinylphenylhydrazide or 1-Phenyl-3 : 6-orthopiperazone 1494
Busch (M.). Synthesis of Ketoquinazolines and Thioquinazolines . . 1495
Fischer (O.) and H. Wreszinski. Action of Formaldehyde on Orthodiamines 1496
Pinner (A.). Nicotine 1497
Hesse (O.). Alkaloïds of Belladonna 1498

PAGE

Schmidt (E.). Hyoscine (Scopolamine) 1498
Schmidt (E.). Berberis Alkaloïds 1498
Link (C.). Berberine and Hydroberberine 1498
Drechsel (E.) and T. R. Krüger. Lysine 1500
Schützenberger (P.). Constitution of Peptones 1500
Ciamician (G.) and C. U. Zanetti. Molecular Weight of the Peptones . 1501
Malfatti (H.). Nuclein 1501
Griffiths (A. B.). Pupin 1501

Physiological Chemistry.

Hugounenq (L.). Influence of Wine on Peptic Digestion 87
Pekelharing (C. A.). Coagulation of the Blood 87
Lepine (R.) and Barral. Hematic Glycolysis: Estimation of Glycogen in the Blood 89
Popoff. Mechanism of the Production of Urea in the Animal Organism . 89
Loew (O.). Action of Azoimide on Living Organisms 90
Landsteiner (K.). Influence of Nutrition on the Composition of Blood Ash 225
Lukjanow (S. M.). Bile during Inanition 225
Treupel (G.). Carbohydrates of Putrefying Human Urine. . . . 226
Rovighi (A.). Ethereal Hydrogen Sulphates in the Urine, and the Disinfection of the Alimentary Canal 226
Laborde (J. V.). Physiological Action of Strontium Salts 227
Schmitt. Physiological Action of Camphors and their Combinations with Chloral 227
Héricort (J.) and C. Richet. Toxic Action of Blood and of various Tissues 228
Charrin (A.). Toxicity of Serum 228
Abelous (J. E.) and F. Heim. Digestive Ferments in Crustacean Eggs . 362
Dastre (A.). Formation of Sugar in the Organism when Oxygen is Deficient 362
Blachstein. Gases of Peptone Blood 363
Glogner (M.). Specific Gravity of the Blood of Europeans living in the Tropics 363
Eijkman (C.). Tropical Anæmia 363
Harley (V.). Disappearance of Sugar from the Blood 363
Lépine (R.) and Barral. Glycolytic Power of Blood and Artificial Production of Diabetes 364
Moitessier (J.). Influence of Muscular Work on the Elimination of Creatinine 364
Colasanti (G.). Xanthocreatinine in the Urine 364
Klingemann (F.). Is Alcohol Eliminated by the Milk? 365
Cornevin (C.). Action of Pilocarpine on the Excretion of Milk . . 365
Herringham (W. P.) and H. O. Davies. Excretion of Uric Acid . . 365
Herringham (W. P.) and E. W. Groves. Excretion of Uric Acid, Urea, and Ammonia 365
Stewart G. N.). Heat Production in Nerves during Excitation . . . 365
Hanriot (M.) and C. Richet. Physiological Action of Nickel Carbon Oxide 365
Langlois (P.). Physiological Action of Nickel Carbon Oxide . . . 365
Combemale and Brunelle. Physiological Action of Trimethylamine . 366
Huber (A.). Physiological Action of Dinitrobenzene 366
Oddo (G.). Relation between the Chemical Constitution and Physiological Action of Aromatic Compounds 366
Tammann (G.). Nasse's Experiments on the Excitabilty of Frog Muscle in Salt Solutions 515
Ellenberger and Hofmeister. Digestion of Starch by Dogs . . . 516
Bunge (G.). The Intake of Iron by the Fœtus 516
Drechsel (E.). Presence of Cystin and Xanthine in the Horse's Liver . 516
Lépine (R.) and Barral. Variations of the Glycolytic and Saccharific Power of Blood in Diseases 517

PAGE

Araki (T.). Formation of Glucose and Lactic Acid 517
Szilasi (J.). Analyses of Human Milk 517
Soxhlet. Sterilisation of Milk 518
Ernst (C.). Putrefaction of Bile 518
Abel (J. J.) and E. Drechsel. Carbamic Acid 518
Roos (E.). Diamines in Disease 518
Jaksch (R. v.). Peptone in the Blood and Organs of Leucæmic Patients . 519
Stone (W. E.). Digestibility of Pentose Carbohydrates 645
Reid (E. W.). Absorption without Osmosis 646
Wright (A. E.). Tissue Fibrinogens 646
Horbaczewski (J.). Formation of Uric Acid from Nuclein . . . 646
Weiske (H.). Influence of Various Salts on Live Weight, and on the Composition of Bones and Teeth 647
Griffiths (A. B.). Blood of Invertebrata 648
Van Nüys (T. C.) and R. E. Lyons. Carbonic Anhydride in the Urine . 649
Hammarsten (O.). Hæmatoporphyrin in Urine 649
Starling (E. H.) and F. G. Hopkins. The Urine in a Case of Phosphorus Poisoning 650
Salkowski (E.). Influence of Amido-acids on Gastric Digestion . . 742
Hanriot. Assimilation of Carbohydrates 742
Gautier (A.). Assimilation of Carbohydrates 742
Gréhant (N.). Absorption of Carbonic Oxide by the Blood of a Living Mammifer 743
Seegen (J.). Sugar in Blood 743
Kornblum (H.). Excretion of Nitrogen in Kidney Disease. . . . 743
Garrod (A. E.). Uro-hæmatoporphyrin 744
Martin (S.). Chemical Pathology of Diphtheria, Anthrax, and Infective Endocarditis 744
Du Bois Reymond (R.). Impure Chloroform 745
Tammann (G.). Unorganised Ferments 899
Jacobson (J.). Unorganised Ferments 899
Artehus (M.). Glycolysis in Blood 900
Berthelot and G. André. Fermentation of Blood 900
Voit (C.), J. G. Otto, A. C. Abbott, G. Lusk, and F. Voit. Formation of Glycogen from Different Sugars 902
Voit (F.). Behaviour of Milk Sugar in a Diabetic 903
Ville (J.). Transformation in the Animal Economy of Sulphanilic Acid into Sulphanilocarbamic Acid 903
Graffenberger (L.). Decomposition of Fibrin, Gelatin, Peptone, and Asparagine in the Human Body 904
Dubelir (D.). Influence of Water and Sodium Chloride on Nitrogenous Excretion 904
Mörner (C. T.). Physiological Action of Gallic and Tannic Acids . . 904
Schmidt (E.). Choline, Neurine, and Allied Compounds 905
Nasse (O.). Physiological Oxidation 1018
Kornauth (C.) and A. Arche. Metabolism in Pigs fed with Corn Cockle. 1018
Krohl (P.). Action of Oxalic Acid and its Derivatives on the Animal Economy 1019
Pekelharing (C. A.). Fibrin Ferment 1112
Griesbach (A.). Coagulation of Blood 1112
Ringer (S.). Calcium Salts and Coagulation 1112
Wright (A. E.). Plasma and Serum 1113
Araki (T.). Formation of Sugar and Lactic Acid in the Organism . . 1113
Young (R. A.). Retiform Tissue. 1113
Koefoed (E.). Acids of Butter 1113
Lassar-Cohn. Presence of Myristic Acid in Ox Gall 1114
Carles (P.). Phosphoric Acid in Urine 1115
Moscatelli (R.). Catechol in the Urine of Hydrophobic Rabbits . . 1115
Schulz (O.). Action of Quinone and its Derivatives 1115
Stackler. Soluble Naphthol Compounds 1116

PAGE

Blum (F.). Thymolglycuronic Acid 1116
Winternitz (H.). Putrefaction of Milk 1116
White (W. H.). Treatment of Chlorosis by Hydrochloric Acid . . . 1117
Martin (S.). Anthrax in Man 1117
Halliburton (W. D.). Mucin in Myxœdema 1117
Sobernheim. Hæmatoporphyrinuria 1118
Kauthack (A. A.). Cobra Poison 1118
Haldane (J.). Respiration Apparatus 1257
Mareš (F.). Formation of Uric Acid in Mammals 1257
Jolyet (F.) and C. Sigalas. Dissolved Nitrogen in Blood . . . 1257
Edkins (J. S.). Absorption of Water from the Alimentary Canal . . 1258
Griffiths (A. B.). Ptomaïnes of Infectious Diseases. 1258
Stutzer (A.). Digestibility of Raw and Boiled Meat 1367
Werigo (B.). Presence of Pentamethylenediamine in Pancreas Extracts . 1368
Tubby (A. H.) and T. D. Manning. Human Succus Entericus . . . 1368
Werigo (B.). Influence of Oxygen in the Separation of Carbonic Anhydride in the Lungs 1369
Bohr (C.). Combination of Hæmoglobin with Oxygen 1369
Janeček (G.). Sensitiveness of the Hæmatin Spectrum and the Formation of Hæmin Crystals as Proof of the Presence of Blood 1369
Fredericq (L.). Hæmocyanin 1370
Cuénot (L.). Respiratory Value of Hæmocyanin 1370
Liebig. Cause of the Rapid Curdling of Milk during Thunder Storms . 1370
Haldane (J.) and J. L. Smith. Air Vitiated by Respiration . . . 1502
Lépine (R.). Formation of Sugar from Peptones in Blood . . . 1502
Bunge (G.). Iron in the Fœtal Organism 1502
Bunge (G.). Iron in the Liver 1503
Amthor (C.) and J. Zink. Horse Fat. 1503
Lassar-Cohn. Myristic Acid in Ox Gall 1503
Formanek (E.). Influence of Hot Baths on the Excretion of Nitrogen and of Uric Acid from the Human System 1503
Gumlich (G.). The Excretion of Nitrogen in Urine 1503
Johnson (G. S.). Reducing Agents in Normal Human Urine . . . 1504
Cohn (R.). Occurrence of Acetyl Derivatives in the Urine of Animals after Ingestion of Aldehydes 1504
Bartoschewitsch (S. T.). Sulphates and Ethereal Hydrogen Sulphates in the Urine during Diarrhœa 1505
Garrod (A. E.). Hæmatoporphyrinuria 1506
Ebstein (W.). Physiological Action of Pentoses. 1506
Paschkis (H.) and F. Obermayer. Pharmacological Investigations of Ketones and Oximes 1506
Smith (W. J.). Physiological Action of Sulphonal 1507
Westberg (A.). Toxic Action of Carbon Bisulphide. 1507

Chemistry of Vegetable Physiology and Agriculture.

Perdrix (L.). A Bacterium which Ferments Starch and Produces Amyl Alcohol 90
Kerry (R.) and S. Fraenkel. Action of the Bacillus of Malignant Œdema on Carbohydrates and on Lactic Acid 91
Monteverde. Influence of Carbohydrates on the Accumulation of Asparagine in Plants 91
Krabbe (G.). Diastase 92
Lesage (P.). Quantity of Starch in the Tubercles of the Radish . . 92
Mueller (C.). Oil of Lime Seed 92
Emmerling (A.). Earth-nut Meal 92
Spica (M.). Behaviour of Strontium Tartrate with Plastered Wines . . 93
Gassend (A.). Presence of Boric Acid in Products of the Soil . . . 93

PAGE

KELLNER (O.), H. SAKANO, D. SATO, and S. SHINJO. Action of Lime as a Manure, with special regard to Paddy Fields 93
MÜNTZ (A.) and A. C. GIRARD. Value of Animal Débris as Nitrogenous Dressing 96
CORNEVIN (C.). Influence of Vegetable Poisons on the Germination of Seeds 228
GRIFFITHS (A. B.). Direct Absorption of Ammoniacal Salts by Plants . 229
HOOPER (D.). Mineral Substance in Teak 230
WARDEN (C. J. H.). Ash of *Achryanthes aspera* 230
BOURQUELOT (E.). Starch in *Boletus pachypus* 230
WEHMER (C.). Formation and Physiological Significance of Oxalic Acid in Fungi 230
LIPPMANN (E. O. v.). Organic Acids in Beet Juice 231
RANSOM (F.). Constituents of Henbane Seed 231
SCHÜTTE (W.). Alkaloïds of the Solanaceæ. 231
INOKO. Toxic Principle of *Amanita pantherina* 232
GLENK (R.). *Cicuta maculata* 232
KRESLING (K.). Pollen of *Pinus sylvestris* 232
TUXEN (C. F. A.). Rain as a source of Nitrogen for Vegetation . . . 233
DEHÉRAIN (P. P.). Phosphoric Acid of the Soil 233
LEONE (T.) and O. MAGNANINI. Nitrification of Organic Nitrogen . . 367
LAWES (Sir J. B.) and J. H. GILBEET. Sources of Nitrogen of our Leguminous Crops 367
FRANK (B.). Assimilation of Free Nitrogen in Plants in its Dependence on Species, on Nutrition, and on Soil 370
IMMENDORFF (H.). The Nitrogen Question 374
SCHLOESING (T., Jun.) and E. LAURENT. Fixation of Free Nitrogen by Plants 378
CHITTENDEN (R. H.) and T. B. OSBORNE. Proteïds of the Maize Kernel . 379
MAXWELL (W.). Choline and Betaïne in Cotton Seed Foods . . . 380
VOSWINKEL (A.) Occurrence of Gums which yield Xylose . . . 380
POULSON (E.). Poisonous Constituent of the Ethereal Extract of Ferns . 380
MARCANO (V.) and A. MUNTZ. Ammonia in the Atmosphere and in Rain Water of the Tropics 381
ALBERT-LÉVY. Ammonia in Rain Water 381
BOURQUELOT (E.). Distribution of Sugar in *Boletus edulis* and *B. aurantiacus* 519
PALLADIN (W.). Amount of Proteïds in Green and in Etiolated Leaves. Acquisition of Green Colour and Growth of Etiolated Leaves . . 520
NILSON (L. F.). Composition of the Leguminosæ 521
GAUTIER (A.) and R. DROUIN. Fixation of Atmospheric Nitrogen by Arable Soils 522
SCHLOESING (T., jun.) and E. LAURENT. Fixation of Free Nitrogen by Plants 523
JOHNSTONE (M.). Fertility of Heavy Loam increased by Lime . . . 532
CHITTENDEN (R. H.), E. P. JOSLIN, and F. S. MEARA. Ferments in Pine-apple Juice 650
MOREL (J.). Action of Boric Acid on Germination 651
LESAGE (P.). Sodium Chloride in Plants 651
WEHMER (C.). Absence of Oxalates in Young Leaves, as in the case of some Phanerogamous Parasites 651
MUSSI (U.). The Latex of *Ficus carica* 653
ORDONNEAU (C.). Cause of Acidity of Green Grapes 653
STONE (W. E.). Constituents of the Nitrogen-free Extract 653
CHATIN (A.). Truffles 654
BERTHELOT and G. ANDRÉ. Spontaneous Oxidation of Humic Acid in Vegetable Soil 655
BERTHELOT and G. ANDRÉ. Estimation of Sulphur in Vegetable Soils and the Forms in which it is Present 656
PICHARD (P.). Influence of the Proportion of Clay and Organic Nitrogen in Fallow Soils on the Absorption of Atmospheric Nitrogen, the Retention of Nitrogen, and Nitrification 656

PAGE

Étard (A.). Compounds that accompany Chlorophyll in Leaves . . 746
Chittenden (R. H.) and T. B. Osborne. Proteïds of Maize . . 746, 749
Wiklund (C. L.). Phosphoric Acid in Soil and its Estimation . . . 750
Effront (J.). New Method of Yeast Purification 905
Effront (J.). Conditions influencing the Action of Fluorides on Fermentation 906
Chuard (E.). Nitrification in Organic Media of Acid Reaction . . . 906
Pichard (P.). Comparative Nitrification of Humus and Undecomposed Organic Matter 906
Viron (L.). Soluble Colouring Matters Produced by Bacteria in Distilled Medicinal Waters 907
Schulze (E.). Vegetable Cell Membranes 907
Vincent (C.) and Delachanal. Occurrence of Mannitol and Sorbitol in the Cherry Laurel 908
Schulze (E.). Occurrence of Guanidine in Plants 908
Roos (L.) and E. Thomas. Vegetation of the Vine 908
Muntz (A.). Ammonia in Rain Water and in the Atmosphere . . . 909
Pagnoul (A.). Experiments on the Growth of Wheat in a Sterile Soil . 909
Beyerinck (M. W.). Accumulation of Atmospheric Nitrogen in Cultivations of *Bacillus radicicola* 1019
Schloesing (T.) and E. Laurent. Fixation of Free Nitrogen by Plants . 1021
Lechartier (G.). Composition and Cultivation of the Jerusalem Artichoke 1024
Sachsse (R.) and A. Becker. Kaolin in Arable Soil 1026
Schmidt (R. H.). Absorption and Digestion of Fat Oils by Plants . . 1118
Hébert (A.). Development of Cereals 1119
Waage (T.). Presence and Function of Phloroglucinol in Plants . . 1120
Osborne (T. B.). Proteïds of the Oat Kernel 1120
Raulin (J.). Influence of the Nature of the Soil on Vegetation . . . 1121
Brown (L. P.). Pea Nut 1122
Schloesing (T.). Fermentation of Farmyard Manure 1123
Bréal (E.). Aërobic Nitrate-reducing Ferment in Straw 1258
Stich. Respiration of Plants under Oxygen Tension, and when Injured . 1259
Bokorny (T.). Nutrition of Green Plant-cells with Formaldehyde . . 1259
Sigmund (W.). Fat-decomposing Ferments in Plants 1261
Löw (O.). Influence of Phosphoric Acid on the Formation of Chlorophyll 1261
Gautier (A.). Origin of the Colouring Matters of the Vine . . . 1262
Lendrich (K.). Constituents of *Menyanthes trifoliata*, and of *Erythræa centaurium* 1262
Pabst (T.). Fruit of *Capsicum annum* 1263
Kraus (G.). Calcium Oxalate in the Bark of Trees 1370
Hébert (A.). Occurrence in Plants of a Gum giving rise to Xylose by Saccharification 1371
Kozai (Y.). Preparation of Teas 1371
Loew (O.). Influence of Phosphoric Acid on the Formation of Chlorophyll 1372
Schutt (F. T.). Analysis of Apple Tree Leaves 1372
Stutzer (A.). Analysis of Healthy and Diseased Sugar Cane . . . 1372
Rodzyanko (A.). Some Properties of Humin and Humic Acid . . . 1373
Frank (B.). To what extent is Atmospheric Nitrogen Assimilable? . . 1507
Bréal (E.). Fixation of Free Nitrogen during Vegetation 1508
Atterberg (A.). Sodium as a Plant Food 1508
Petit (P.). Distribution and Condition of Iron in Barley 1509
Weber (J.). Oil of Cinnamon 1509
Kwasnik (W.). Crystalline Constituent of *Genipa brasiliensis* . . . 1509
McBryde (J. B.). Chemical Study of the Cotton Plant. Feeding Value of the Cotton Plant 1510
Jaffa (M. E.). Composition of the Ramie Plant (*Boehmeria*) . . . 1511
Colby (G. E.) and H. L. Dyer. Analyses of California Oranges and Lemons 1511
Stutzer (A.). Food Value of Brushwood 1511
Stutzer (A.). Composition of Frozen and Unfrozen Beet-chips . . . 1512

PAGE

Schmitter. Experiments on Soil Inoculation 1512
De Mondesir (P.). Inorganic Acid Substance in Soils 1513

Analytical Chemistry.

Boas (J.). Estimation of Hydrochloric Acid in Gastric Juice . . . 97
De Koninck (L. L.). Estimation of Free Oxygen by means of Nitric Oxide 97
Kisch (W.). Estimation of Free Oxygen dissolved in Water . . . 98
König (J.). Schützenberger's Process for the Estimation of Free Oxygen . 98
Jones (R.). Analysis of Phosphates 99
Gréhant (N.). Detection of Minute Quantities of Carbonic Oxide . . 99
Fresenius (R.). Separation of Barium from Calcium 100
Adeney (W. E.) and T. A. Shegog. Combination of Wet and Dry Methods in Chemical Analysis 100
Regelsberger (F.). Assay of Commercial Aluminium 102
Drown (T. M.) and G. A. McKenna Direct Estimation of Aluminium in Iron and Steel 102
Campbell (A. C.). Separation of Iron from Cobalt, Nickel, and Manganese 103
Baumann (A.). New Method of Quantitative Analysis 103
Gossart (E.). Application of Capillary Phenomena to the Analysis of Liquids 236
Graffenberger (L.). Estimation of Free Hydrochloric Acid in the Stomach 236
Gooch (F. A.) and C. G. Smith. Estimation of Chlorates 236
Denigès (G.). Microscopic Detection of Sulphurous Anhydride. . . 237
Boyer (E.). New Method for the Estimation of Nitrogen 237
Blair (A. A.). Estimation of Carbon in Steel 237
Baubigny (H.). Estimation of Thallium 238
Smith (E. F.) and D. L. Wallace. Oxidation of Copper Glance by the Electric Current 239
Smith (E. F.) and A. W. MacCauley. Electrolytic Separation of Mercury from Copper 239
Plugge (P. C.). Reaction for Cerous Oxide 239
Jannasch (P.) and C. J. Franzek. Separation of Manganese and Nickel, and Cobalt 240
Namias (R.). Volumetric Estimation of Iron 240
Lapicque (L.). Colorimetric Estimation of Iron. 240
Jannasch (P.) and H. Vogtheer. Decomposition of Chrome Iron Ore by Hydrochloric Acid under pressure 240
Smith (E. F.) and R. H. Bradbury. Estimation of Molybdic and Tungstic Acids 241
Gooch (F. A.) and H. W. Gruener. Estimation of Antimony . . . 242
Mason (W. P.). Carbazole Method for the Estimation of Nitrates in Water Analysis 243
Hazen (A.) and H. W. Clark. Estimation of Nitrates in Water . . 243
Cripps (R. A.). Estimation of Volatile Oil in Copaiba 244
Allen (A. H.) and W. Chattaway. Examination of Spirits for Secondary Constituents 244
Jean (F.). Estimation of Glycerol, Astringent Acids, and Colouring Matter in Wine 246
Stone (W. E.). Estimation of Pentoses in Vegetables. 247
Wiechmann (F. G.). Estimation of Mixtures of Saccharose, Fruit-sugar, and Dextrose, or Levulose 248
Elion (H.). Estimation of Maltose, Dextrose, and Dextrin in Beer Wort . 248
Obermüller (K.). Estimation of Chlolesterol 248
Tollens (B.) and others. Carbohydrates 248
Thoms (H.). Valuation of Oil of Cloves 250
Sykes (W. J.). Examination of Vinegar 251

PAGE

Buisine (A.) and P. Buisine. Adulteration of Beeswax 251
Crismer (L.). Test for Hydrogen Peroxide 381
Wilson (J. M.). Standardising Iodine Solutions for the Estimation of Sulphur in Steel, &c. 382
Craig (G.). Estimation of Sulphur 382
Angeli (A.). Estimation of Sulphur in Organic Substances . . . 382
Edwards (V.). Estimation of Phosphoric Acid in Slags 382
Sanger (C. R.). Estimation of Arsenic in Wall Paper 382
Hehner (O.). Estimation of Boric Acid 384
Wilson (J. A.). Estimation of Combined Alkali in Soap 384
Donath (E.). Separation of Manganese and Zinc 384
Norris (G. L.). Estimation of Manganese in Slags and Ores . . . 385
Jannasch (P.) and P. Etz. Separation of the Metals of the Hydrogen Sulphide Group by Means of Bromine Vapour 385
Remmler (W.). Separation of Bismuth and Lead 385
Crismer (L.). Reaction of Certain Essences with Manganous Salts . . 386
Crismer (L.). Detection of Turpentine and other Impurities in Essences . 386
Bell (J.). Analysis of Spirits 387
Schmoeger (M.). Estimation of Sugars by Means of Ost's Copper Solution 387
Babington (F. W.). Analysis of Sugar, Wine Molasses, and Syrup . . 388
Günther (A.), G. de Chalmot, and B. Tollens. Estimation of Furfuraldehyde and of Pentoses 388
Kobert (R.). Detection of Hydrogen Cyanide 389
Twitchwell (E.). Estimation of Resin in its Mixtures with Fatty Acids . 389
Hinsdale (S. J.). Estimation of Gallotannic Acid, Gallic Acid, and Tannin 390
Hill (T. E.). The Werner-Schmid Method of Milk Analysis . . . 390
Stokes (A. W.). Extraction of Fat from Milk Solids. 391
Muter (J.). Detection of Cocoa-nut Fat in Butter 391
Lezé and Allard. Estimation of Fat in the Products from Milk . . 391
Allen (A. H.). Assay of Aconite Preparations 392
Hempel (W.). New Desiccator 524
Lunge (G.). Improvement in Gas-volumetric Apparatus 524
Bailey (G. H.) and J. C. Cain. Simple and Rapid Method of Gravimetric Analysis. 524
Bornträger (A.). Use of Potassium Hydrogen Tartrate in Titrating Standard Acids and Alkalis 525
Quincke (J.). Gasometric Alkalimetry and the employment of Potassium Ferricyanide in Gasometry 526
De Koninck (L. L.) and E. Nihoul. Estimation of Soluble Chlorides, Bromides, and Iodides 527
Smith (J. H.). New Method for Estimating Organic Nitrogen . . . 527
Fricke (E.). Estimation of Nitrogen in Nitrates 527
Süllwald (A.). Estimation of Nitrogen in Pure and Mixed Nitrates. . 528
Malot (C.). Estimation of Phosphorus in Iron and Steel 528
Emmerton (F. A.). Estimation of Phosphorus in Pig-Iron, Steel, and Iron Ores 529
Haack (K.). Separation of Phosphoric and Arsenic Acids from Mercury, and of Nitric Acid, Chlorine, and Sodium from Mercury, Phosphoric, and Arsenic Acids. 530
Clark (J.). Direct Estimation of Arsenic in Minerals and Metals . . 530
Lunge (G.) and L. Marchlewski. New Apparatus for the Estimation of Combined and Free Carbonic Acid 531
Schulz (O.). Apparatus for the Estimation of Carbonic Anhydride in Air . 533
Vogel (J. H.). Estimation of Lime in Phosphates by Glaser's Process . 534
Blum (L.). Volumetric Estimation of Zinc. 534
Wells (J. S. C.). Separation of Copper and Cadmium 534
Regelsbeeger (F.). Assay of Aluminium and its Alloys 535
Cross (C. F.) and E. J. Bevan. Volumetric Estimation of Alumina . . 535
Lunge (G.). Volumetric Estimation of Alumina 535

PAGE

Kretzschmar (M.). Commercial Assay of Alums 535
Meyer (T.). Estimation of Iron and Alumina in Phosphates . . . 536
Pattinson (J.) and H. S. Pattinson. Estimation of Manganese in its Ores and Alloys 536
Jannasch (P.) and R. Niederhofheim. Separation of Metals in Alkaline Solution by Hydrogen Peroxide 537
De Koninck (L. L.) and M. Ledent. Action of Alkali Sulphides on Metals of the Iron Group 537
Hogg (T. W.). Estimation of Chromium in Steel 538
Baumann (A.). Gas-volumetric Analysis 538
Lunge (G.). Gas-volumetric Analysis 538
Baumann (A.). New Methods in Quantitative Analysis 538
Namias (R.). Estimation of Tungsten in Rich Alloys and in Steel . . 539
Wells (J. S. C.). Analysis of Tin Ores 540
Jannasch (P.) and P. Etz. Separation of Metals of the Hydrogen Sulphide Group by means of Bromine Vapour 540
Kohn (C. A.). Application of Electrolysis to Qualitative Analysis . . 540
Gooch (F. A.) and E. W. Danner. Separation of Antimony from Arsenic 541
Archarow (J.). Estimation of Organic Matter in the Atmosphere . . 542
Gray (J.). Apparatus for Determining the Flashing Point of Heavy Mineral Oils 542
Blunt (T. P.). Indirect Estimation of Alcohol 543
Traube (J.). Estimation of Fusel Oil in Spirits 543
Bornträger (A.). Decolorisation of Wines 543
Bader (A.). Alkalimetric Estimation of Phenol 543
Rumpf. Estimation of Phenols in Human Urine. 544
Lewkowitsch (J.). Estimation of Cholesterol 544
Johnstone (W.). Estimation of Glycerol by Alkaline Permanganate . . 544
Filsinger (F.). Analysis of Crude Glycerol 544
Bourquelot (E.). Detection and Extraction of Trehalose 545
Strache (H.). Estimation of Aldehydic and Ketonic Oxygen . . . 546
Wilson (J. A.). Separation of Resin from Fatty Acids 546
Crismer (L.). Detection of Tartaric Acid in Citric Acid 546
Groves (E. W.). Estimation of Uric Acid 546
Thomson (R. T.) and H. Ballantyne. Revision of Constants employed in the Analysis of Fats and Oils 547
Grittner (A.). Detection of Resin Oil in Fatty and Mineral Oils . . 548
Gottlieb (E.). Estimation of Fat in Milk 549
Nilson (L. F.). The Lactocrite compared with other Methods for Estimating Fat in Milk 550
Szilasi (J.). Milk Analysis. 550
Pinette (J.). Soap Analysis 550
Röttger (H.). Assay of Bees Wax for Vegetable Wax 551
MacWilliam (J. A.). Salicylsulphonic Acid as a Test for Albumoses and Peptones. 552
Sauer (E.). New Drying Apparatus for Elementary Analysis . . . 657
Gigli (T.). Estimation of Iodates in Potassium Iodide 657
Bosio (G.). Influence of Temperature on Griess' Reaction for Nitrites in Water 657
Jannasch (P.) and V. Wasowicz. Estimation of Sulphur in Inorganic Sulphides. Analysis of Molybdenite, Realgar, and Orpiment . . 657
Jannasch (P.) and K. Aschoff. Estimation of Sulphur in Galena and Minerals containing Lead 658
Berthelot and André. Estimation of Sulphur in Vegetable Soils . . 659
Cazeneuve (P.) and Nicolle. Rapid Estimation of Sulphuric Acid . . 659
Kubel (W.). Analysis of Carlsbad Salt 659
Fileti (W.). Analysis of the Barium Group 660
Lainer (A.). Estimation of Silver and Gold by means of Hydroxylamine Hydrochloride 662
Jannasch (P.) and K. Aschoff. Analysis of Galena 662

PAGE

JANNASCH (P.) and T. BICKES. Analysis of Galena 663
NAMIAS (R.). Volumetric Estimation of Mercury 663
LACHAUD and LEPIERRE. Analysis of Chrome Yellows 663
JONES (J.). Decomposition of Minerals containing Titanium . . . 664
BERTRAND (G.). Colour Reactions of Carbohydrates 664
HAINES (R.). Iodine Number for Lard Oil by the Hübl Method. . . 664
GRIPPER (H.). Rapid Method of Determining the Composition of Lubricating Oils 665
BUCHNER (G.). Analysis of White Wax 665
SESTINI (F.) and R. CAMPANI. Detection of Quinine and Phenacetin in Urine 665
MANSEAU (M. H.). Detection and Estimation of Santonine . . . 666
CHRISTENSEN (A.). Estimation of Free Alkaloïds and their Molecular Weight 666
WHITELEY (R. L.) and J. T. WOOD. Löwenthal's Method of Tannin Analysis 667
CROCCO (P.). Detection of Albumin in Urine 667
FUBINO (S.). Detection of Vegetable Fibre in Silk or Woollen Tissue. 667
WARREN (T. T. P. B.). Valuation of Coal for Use in Steam Boilers . . 668
BARBA (W. P.). Asbestos in Filtration 751
VOORHEES (E. B.). Estimation of Nitrogen 751
GREEN (A. G.) and F. EVERSHED. Estimation of Nitrous Acid . . . 751
FRANKEL (L. K.). Oxidation of Arsenic by the Electric Current . . 752
WIKLUND (C. L.). Estimation of Phosphoric Acid in Soils. . . . 753
LOBRY DE BRUYN (C. A.). Estimation of Sulphur in Red Copper . . 753
BERTHELOT. New Method of Organic Analysis 753
GIBBS (W.). Electrolytic Estimation of Metals as Amalgams . . . 753
LOBRY DE BRUYN (C. A.) and F. H. VAN LEENT. Estimation of Copper . 753
JANNASCH (P.) and P. ETZ. Separation of the Metals of the Hydrogen Sulphide Group by means of Bromine Vapour 754
GIBBINS (B. H.). Estimation of Iron and Aluminium by the Glaser Method 755
KRUG (W. H.). Estimation of Iron and Aluminium in the presence of Phosphoric Acid 755
VITALI (D.). Reactions of Hydrastine and other Alkaloïds. . . . 755
WILLARD (J. T.) and G. H. FAILYER. Extraction Apparatus . . . 910
FEIT (W.) and K. KUBIERSCHKY. Use of Bromic Acid in Quantitative Analysis 910
CARNOT (A.). Estimation of Fluorine 911
HAMILTON (R.). Precipitation of Phosphorus from Solutions of Iron and Steel 911
REINHARDT (C.). Estimation of Phosphorus in Pig Iron by means of Braun's Centrifugal Apparatus 912
SPICA (M.). Volumetric Estimation of Phosphoric Acid 912
VOGEL (J. H.). Analysis of Phosphates 912
THÖRNER (W.). Estimation of Carbon in Iron and Steel 913
GOOCH (F. A.) and T. S. HART. Detection and Estimation of Potassium Spectroscopically 913
KRÜGER (M.). Estimation of Small Quantities of Calcium 914
FRESENIUS (W.) and F. RUPPERT. Solubility of Calcium and Strontium Chromates in Dilute Alcohol, and the Separation of these Metals as Chromates 914
BROWNING (P. E.). Separation of Strontium and Calcium Nitrates by means of Amyl Alcohol 915
BROWNING (P. E.). Separation of Barium from Calcium 915
MOLDENHAUER (F.). Estimation of Zinc by the Ferrocyanide Process . 915
RÜRUP (L.). Estimation of Manganese in Iron and Steel 916
RIGGS (R. B.). Separation of Iron, Manganese, and Calcium . . . 916
SMITH (E. F.) and F. MUHR. Electrolytic Separation of Iron . . . 917
MOORE (T.). Estimation of Cobalt in Manganese Ores. 917
PÉCHARD (E.). Estimation of Molybdenum. 917

PAGE

Pieszczek (E.). Detection of Tin, Antimony, and Arsenic. . . . 918
Carnot (A.). Assay of Antimony Minerals. 918
Hampe (W.). Estimation of Bismuth in Silver Slags 919
Whitehead (C.). Use of Cadmium in Assaying Gold 919
Smith (E. F.) and D. L. Wallace. Electrolytic Separations . . . 920
Mylius (F.) and F. Foerster. Assay of Platinum 920
Hazen (A.). Estimation of the Dissolved Matter in Water. . . . 920
Young (W. C.). Volatile Organic Matter in Potable Water: Method of Estimating Dissolved Fixed and Volatile Organic Matter in Water . 921
Medicus (L.) and C. Immerheiser. Fermentability of Dextrins . . 922
Fresenius (W.). Recognition of Potato Starch Sugar in Wines. . . 922
Gabriel (S.). Estimation of Cellulose 923
Zune. Detection of Resin Oil in Terebenthene 923
Röttger (H.). Detection of Resin in Beeswax 923
Bittó (B. v.). Sodium Nitroprusside as a Reagent for Aldehydes and Ketones 924
Schimmel. Estimation of Cinnamaldehyde. 924
Besana (C.). Estimation of Free Acids in Butter 924
Mörner (C. T.). Estimation of Gallic Acid in Urine. 924
Baumann (E.). Estimation of Homogentisic Acid in the Urine . . . 925
Raabe (F. F.). Assay of Commercial Toluidine 925
Schulze (E.). Test for Guanidine 996
Doet (D. B.). Assay of Opium 926
Domergue (A.) and C. Nicolas. Analysis of Tea 926
Procter (H. R.). Analysis of Gambier 928
Spiegler (E.). Sensitive Reaction for Albumin in Urine 928
Reid (A. F.). Improvements in Burettes 1027
Schwicker (A.). Use of Iodic and Bromic Acids in Quantitative Analysis 1027
Schierholz (C.). Separation of Iodine, Bromine, and Chlorine. . . 1028
Lunge (G.). Analysis of Sodium Nitrite 1029
Dancy (F. B.). Estimation of Phosphoric Acid in Fertilisers . . . 1029
Sautermeister (O.). Testing Metallic Iron for Arsenic 1030
Jüptner (H. v.). Wiborgh's Gasometric Method for the Estimation of Carbon in Iron 1030
French (W.). Estimation of Gold, Tin, and Cadmium in Alloys . . 1030
Rubricius (H.). Estimation of Manganese in Iron and Steel . . . 1030
Donath (E.). Analytical Application of Barium and Hydrogen Peroxides. 1031
Sachsse (R.) and A. Becker. Estimation of Kaolin in Arable Soils . . 1031
Grünhut (L.). Rose's Process for the Estimation of Alcohol . . . 1031
Wilson (J. A.). Action of Alkaline Mercuric Cyanide on Maltose, Dextrose, and Dextrin 1032
Schwicker (A.). New Reagent for Acetone 1032
Geelmuyden (H. C.). Estimation of Uric Acid. 1032
Balli (B.). Estimation of Cream of Tartar in Wine Lees. 1033
Rodewald (H.). Detection of Margarine in Butter 1034
Mangold (C.). Analysis of Beeswax 1034
Schlicht (A.). Estimation of Oil of Mustard 1035
Prelinger (O.). Picric Acid as a Test for Guanidine. 1036
De Chardonnet. Specific Gravity of Fibres 1036
Vignon (L.). Specific Gravity of Silk. 1036
Winternitz (H.). Colour Reactions of the Proteïd Precipitate produced by Potassium Ferrocyanide 1036
Gill (A. H.). Improved Pipette for Gas Absorptions 1124
Denigès (G.). Preservation of Solutions of Metaphenylenediamine and its Employment as a Reagent 1124
Langermann (G.). Estimation of Hydrochloric Acid in the Contents of the Stomach 1125
Edwards (V.). Estimation of Nitrogen 1125
Burney (W. B.). Estimation of Phosphoric Acid 1125

PAGE

Gibson (C.). Differences in the Estimation of Reverted Phosphoric Acid by the American Official Method 1126
Huston (H. A.). Action of Ammonium Citrate on High Grade Aluminium Phosphate 1127
Hampe (W.). Estimation of Silicic Acid in Fluorides 1127
Regelsberger (F.). Estimation of Silicic Acid in Fluorides . . . 1128
De St.-Martin (L.). Estimation of Carbonic Oxide 1128
Luckow (C.). Volumetric Estimations and Separations by means of Potassium Ferrocyanide and Ferricyanide 1129
Patein (G.). Detection of Normal Carbonate in Hydrogen Alkali Carbonates 1130
Hunt (A. E.), G. H. Clapp, and J. O. Handy. Analysis of Aluminium . 1130
Hampe (W.). Estimation of Manganese by the Chlorate Method . . 1132
Reis (M. A. v.). Estimation of Manganese by the Chlorate Method . . 1132
Riban (J.). Colorimetric Estimation of Iron 1132
Terreil. Nickel and Cobalt Reactions 1132
McCay (L. W.). Test for Chromium 1133
Stahl (J.). Molybdic Acid as a Reagent for Aromatic Hydroxy-compounds 1133
Haig (A.). Estimation of Uric Acid 1133
Gassend (A.). Detection of Sesame Oil in Olive Oil 1133
Welmans (P.). Detection of Vegetable Oils in Lard 1133
Pinette (J.). Estimation of Fat in Milk by Schmid's Method . . . 1134
Bein (S.). Estimation of Fat in Yolk of Eggs 1134
Crafts (J. M.). Separation of the Xylenes 1134
Moitessier (J.). Estimation of Creatinine in Urine 1135
Fleury (G.). Estimation of Tannin 1135
Étard (A.). Method of Analysis of Chlorophyllic Extracts. Nature of Chlorophyllane 1136
Riva-Rocci (S.). Estimation of Peptones in the Stomach Contents . . 1136
Hammarsten (O.). Detection of Hæmatoporphyrin in Urine . . . 1136
Lecco (M. T.). Estimation of Glycerol in Sweet Wines 1263
Bittó (B.v.). Behaviour of Aldehydes and Ketones with Aromatic Nitrocompounds 1263
Roux. Volumetric Estimation of Peptones in Urine 1264
Hoppe-Seyler. Colorimetric Estimation of Hæmoglobin 1264
Gill (A. H.). Improved Gas Pipette 1374
Lieben (A.). Errors arising in Chemical Operations owing to the Employment of Gas Flames 1374
Namias (R.). Extended Employment of Arsenious Acid in Volumetric Analysis 1374
Blum (L.). Presence of Lead in Glass Wool 1375
Glaser. Gasometric Estimation of Nitric Acid 1375
Treadwell (F. P.). Estimation of Sulphur 1375
Blum (L.). Absorption Apparatus for Use in the Estimation of Sulphur in Iron 1376
Freund (E.). Volumetric Estimation of Sulphuric Acid in Urine . . 1377
Bouriez (A.). Volumetric Estimation of Sulphides 1377
Wolf (J.). Estimation of Calcium Salts in Syrup and Sugar Products . 1377
Aubin (E.). Separation and Estimation of Lead, Silver, and Zinc in Galena and Blende 1378
Mesnard (E.). Essence of Sandal Wood 1379
Bardy (C.). Detection of Higher Alcohols in Spirits of Wine . . . 1379
De Coninck (O.). Reactions of Amidobenzoic Acids 1380
Forbes (M.). Apparatus for Washing Precipitates 1513
Fuchs (F.). A New Combustion Furnace 1514
Salzer (T.). Iodometry 1514
Macnair (D. S.). Detection of Chlorine and Bromine in presence of Iodine 1514
Vitali (D.). Volumetric Estimation of Soluble Sulphides 1515

PAGE

Farnsteiner (K.). Volumetric Estimation of Combined Sulphuric Acid . 1515
Blau (F.). Estimation of Nitrogen in Organic Substances 1515
Stock (W. F. K.). Estimation of Nitrogen in Organic Substances . . 1516
Arnold (C.) and K. Wedemeyer. Boyer's Method of Estimating Nitrogen 1517
Arnold (C.) and K. Wedemeyer. Estimation of Nitrogen in Nitrates . 1517
Ulsch (K.). Action of the Copper-Iron Couple on Nitrates and Nitrites . 1518
Foerster (O.). Estimation of Phosphoric Acid by the Molybdate Process . 1519
Franceschi (G.). Volumetric Estimation of Arsenic Acid 1519
McCay (L. W.). Separation of Thioarsenic and Thioxyarsenic Acids . . 1519
Westberg (A.). Toxic Action and Detection of Carbon Bisulphide . . 1520
Schjerning (H.). Estimation of Calcium and Magnesium in Guncotton . 1520
Vitali (D.). Volumetric Estimation of the Metals of the Alkaline Earths and of some Heavy Metals 1521
Freudenberg (H.). Electrolytic Separation of Metals 1521
Benedikt (R.). Analysis of Galena and Lead Sulphate 1522
Benedikt (R.) and L. Gans. Separation of Silver and Lead . . . 1522
Medicus (L.). Estimation of Lead 1522
De Colli (N.). Detection of Alum in Wines 1523
Glaser (C.). Estimation of Aluminium Phosphate 1523
Rubricius (H.). Estimation of Manganese in Iron 1524
Grützner (B.). Stability of Potassium Permanganate 1524
Huppert. Hamburger's Method for the Estimation of Small Quantities of Iron 1525
Hambly (F. J.). Detection of Nickel and Cobalt 1525
Waller (E.) and H. T. Vulte. Analysis of Chromite 1525
Whitehead (C.). Estimation of Small Quantities of Gold and Silver in Base Metals 1525
Franceschi (G.). Volumetric Estimation of Gold 1526
Hollemann (A. F.). Testing the Purity of Platinic Chloride . . . 1526
Hoppe-Seyler (F.). Extraction of the Dissolved Gases in Water . . 1526
Hazen (A.). New Colour Standard for Natural Waters 1527
Luckow (C.). Volumetric Analyses by means of Potassium Ferrocyanide and Ferricyanide 1527
Richmond (H. D.). Estimation of Iodoform 1528
Benedikt (R.) and J. Neudörfer. Oxidation of Alcohol by Permanganate 1529
Baumert (G.). Estimation of Glycerol in Wine 1529
Hoppe-Seyler (G.). Test for Sugar in Urine 1529
Strache (H.). Improvement in the Method of Estimating Aldehydic and Ketonic Oxygen 1530
Tcherniac (J.). Estimation of Thiocyanacetone 1530
Venturoli (G.). Estimation of Hydrocyanic Acid 1530
Micko (C.). Separation of Malic Acid from Succinic, Citric, and Tartaric Acids 1531
Ackermann (E.). Estimation of Tartar in Sweet Wines 1531
Schaap (Miss J.). Separation of Salicylic from Benzoic Acid . . . 1532
Leffmann (H.) and W. Beam. Estimation of Fat in Milk 1532
Erdélyi (J.). Detection of Foreign Fats in Butter 1532
Amthor (C.) and J. Zink. Horse Fat 1533
Mansbridge (W.). Estimation of Unsaponifiable Matter in Fats . . 1533
Drechsel (E.). New Reaction of Xanthine and Allied Compounds . . 1534
Fabris (L.). Detection of Atropine 1534
Moscheles and Stelzner. Analysis of Coffee Substitutes 1534
Hiltner (L.). Approximate Estimation of Adulteration of Earth-nut Cake and Meal 1535
Heaton (C. W.) and S. A. Vasey. Analysis of Peptones 1535

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

---

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+2}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus: $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = α-dimethylethylene; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{:}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{:}C{\cdot}C_nH_{2n+1}$. Adopt the same *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol: furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2\cdot COOH$, and not $C_6H_3(OC_2H_5)_2\cdot COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2\cdot NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2\cdot CH_2\cdot CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO\cdot CH_3$, and Bz for $CO\cdot C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3\cdot CH(OEt)_2$ instead of $CCl_3—CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$

$[CCl_3\cdot CH(OH)]_2S$ instead of $\begin{matrix}CCl_3—CHOH\\CCl_3—CHOH\end{matrix}>S$

$CH_2 : CH_2$ instead of $CH_2=CH_2$

$CH : CH$ instead of $CH\equiv CH$

$CH : C\cdot CH_2\cdot CH_2\cdot C : CH$ instead of $\begin{matrix}CH_2—C\equiv CH\\|\\CH_2—C\equiv CH\end{matrix}$

$CHMe : CHPr^{\alpha}$ instead of $CH_2\cdot CH=CH\cdot CH_2\cdot CH_2\cdot CH_3$

$COOH{\cdot}CH : CMe{\cdot}COOH$ instead of $\begin{matrix} CH_3{-}C{=}CH \\ \quad\;| \quad\;| \\ COOH \quad COOH \end{matrix}$

$CH_2Br{\cdot}CBrMe$ instead of $\begin{matrix} CH_3CH_3 \\ \quad\diagdown\diagup \\ \quad CBr \\ \quad\;| \\ \quad CH_2Br \end{matrix}$

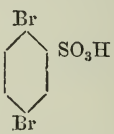
$CEt_2Ac{\cdot}COOEt$ instead of $\begin{matrix} CH_3 \\ \;| \\ CO \\ \;| \\ C{<}\begin{matrix}C_2H_5\\C_2H_5\end{matrix} \\ \;| \\ COOC_2H_5 \end{matrix}$

$\begin{matrix} CH_2{\cdot}CHMe \\ | \\ CH_2{\cdot}CHMe \end{matrix}{>}O$ instead of $\begin{matrix} CH_2{-}CH{\cdot}CH_3 \\ \;| \qquad\diagup \\ \;| \qquad O, \\ \;| \qquad\diagdown \\ CH_2{-}CH{\cdot}CH_3 \end{matrix}$

$CHPh(OBz){\cdot}CH(OBz){\cdot}COOEt$ instead of
$C_6H_5{\cdot}CH(O{\cdot}CO{\cdot}C_6H_5){\cdot}CH(O{\cdot}COC_6H_5){\cdot}COOC_2H_5$.

19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2{\cdot}SO_3H[Br : SO_3H : Br =$

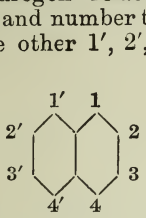
1 : 2 : 4] instead of 

the figures always being used in the order 

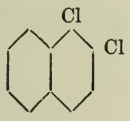
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

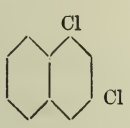
In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—

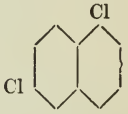


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—

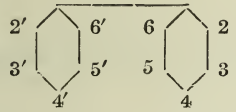
1 : 2 dichloronaphthalene = 

1 : 1′ dichloronaphthalene = 

1 : 3 dichloronaphthalene = 

1 : 3′ dichloronaphthalene = 

In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′. as shown by the following symbol:

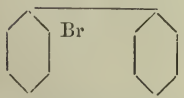


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
„ [Br = 3]
„ [Br = 4]

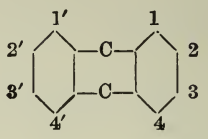
and the two dibromodiphenyls 

and



are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6′].

In the case of anthracene, employ the following symbol, and indicate the position of the radicles relatively to the central C_2-group:



Examples:

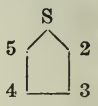
Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].
Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

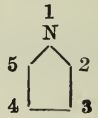
1 : 2 Dihydroxyanthraquinone		= Alizarin.
1 : 4	,,	= Quinizarin.
2 : 3′	,,	= Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone		= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

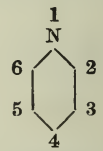
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

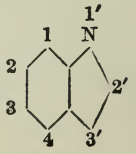


Pyrroline.

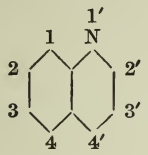


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

38608

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Refraction and Dispersion of Sodium Chlorate. By F. Dussaud (*Compt. rend.*, **113**, 291—292).—The measurements were made with several different forms of refractometer, but the divergences between the results obtained with different instruments did not seem to follow any definite law. The following are the indices of refraction at 23°:—

a.	B.	C.	D.	*b*.	F.
1·51097	1·51163	1·51267	1·51510	1·51933	1·52161

Cd_9.	Cd_{10}.	Cd_{11}.	Cd_{12}.	Cd_{17}.	Cd_{18}.
1·53883	1·54242	1·54421	1·54700	1·57203	1·58500

The mean variation of the index of refraction is −0·000057 per degree, and seems to be practically the same for all the visible rays.

C. H. B.

Relation between the Index of Refraction, Density, Molecular Weight, and Diathermanous Power of a Substance. By Aymonnet (*Compt. rend.*, **113**, 418—421).—If A is the diathermanous conductivity of a certain substance, $A = \frac{1}{2}MV^2$, where M is the mass contained in unit area of substance of thickness $k\lambda$, and V is the mean velocity. $M = k\lambda d$, d being the density of the liquid. If k is proportional to the thickness ϵ of a molecule, $k = C\epsilon$, where C is a constant. If the molecule is spherical, $\epsilon = (e/d)^{\frac{1}{3}}$, e being the molecular weight. Suppose $V = n - 1$, where n is the index of refraction, then

$$AP = \tfrac{1}{2}Ce^{\frac{1}{3}}d^{\frac{2}{3}}(n-1)^2\lambda,$$

where P is a correction applied on account of reflection.

The author verifies the above formula by observations with water, alcohol, benzene, chloroform, and carbon bisulphide. H. C.

Emission Spectra of Neodymium and Præseodymium Oxides and of Luminous Solids containing Neodymium. By L. Haitinger (*Monatsh.*, **12**, 362—367).—Welsbach found that præseodymium oxide gives a continuous emission spectrum, and neodymium oxide a discontinuous spectrum similar to that noticed by Bunsen in the case of didymium oxide. The author confirms Welsbach's observations with neodymium oxide, using this oxide mixed with aluminium oxide for the production of the spectrum. The lines are found to vary somewhat, both in intensity and position, on long-continued heating of the mixed oxides, and also if magnesium is substituted for aluminium oxide. Præseodymium oxide, which alone has no emission spectrum, shows one when mixed with aluminium oxide. This behaviour may, perhaps, be explained by assuming that a higher oxide is formed when the salt is heated alone, but not when mixed with other oxides. No emission spectrum was, however, obtained on heating præseodymium oxide in a reducing atmosphere. The presence of a trace of neodymium in calcium sulphide causes a phosphorescence, the spectrum of which is similar to the absorption spectrum of concentrated solutions of neodymium salts. H. C.

Study of the Chemical Neutralisation of Acids and Bases, by means of their Electrical Conductivities. By D. Berthelot (*Compt. rend.*, **113**, 261—263).—A summary of the results of the researches previously published. Potassium hydroxide, a strong base, with hydrochloric acid, acetic acid, or phenol gives compounds which have almost identical conductivities, behave as true salts, are stable in solution, and are not decomposed by water. Ammonia, a feebler base, with hydrochloric acid and acetic acid gives stable compounds, but with phenol only an unstable compound with a higher resistance than the normal salts, and, to a large extent, dissociated by water. Aniline, a still feebler base, gives with hydrochloric acid a stable compound that is a good conductor; with acetic acid an unstable compound with a considerably higher resistance; and with phenol only a non-conducting mixture without any trace of combination.

Experiments with the hydroxybenzoic acids, which unite the functions of an acid and a phenol, show that, whilst the presence of the two functions can be readily recognised, they affect one another in a manner more or less marked according to their relative positions in the molecule. C. H. B.

Calculation of the Specific Heat of Liquids. By G. Hinrichs (*Compt. rend.*, **113**, 468—471).—In the liquid state, molecules rotate round the natural axis, for which the moment of inertia is a minimum. If i is the moment of inertia, M the mass of the molecule, and ρ the radius of gyration, $i = M\rho^2$. The total energy, ϵ, of the molecule of a liquid is the sum of the energy of rotation and of the potential energy, which is a function ϕ of the absolute temperature T,

$$\epsilon = kiT + M\phi(T) = Me,$$

where $e = k\rho^2 T + \phi(T)$, the total energy of unit mass. The specific heat, c, of unit mass will be obtained by differentiation of e with regard to T,

$$c = K\rho^2 + \phi'(T).$$

The author shows that a formula of this kind holds in the case of the ethereal salts of the fatty acids, taking Schiff's observations of the specific heats of salts of this series. H. C.

Second Law of Thermodynamics and its Application to Chemical Phenomena. By H. Le Chatelier (*Bull. Soc. Chim.* [3], **5**, 837—840).—Carnot's principle is directly applicable to chemical changes, if all restriction as to the nature of the equilibrium established by the change is removed. The same reasoning which is applied to the establishment of heat equilibrium may then be applied to chemical equilibrium. The available energy obtainable from two different states of the same system will be the same for all reversible transformations of the one state into the other, and independent of the means employed for rendering this energy available, and will be greater for reversible than for non-reversible transformations. The author shows how from this principle may be deduced, in a very simple manner, the laws of isodissociation which he formerly obtained by a far more complicated process—starting from the two equivalent principles of Clausius. H. C.

New Isothermal Curves for Carbonic Anhydride. By E. H. Amagat (*Compt. rend.*, **113**, 446—451).—The author has determined the isothermals for carbonic anhydride for every 10° from 0° to 100°, and also for the temperatures 32°, 35°, 137°, 198°, and 258°. The pressures were taken up to 1000 atmospheres, and the method employed was that described in former communications. The results are given in tabular form, and the isothermal curves for each of the temperatures taken. The following table is given for the pressures of liquefaction of carbonic anhydride at the temperatures under examination :—

Temperature.....	0°	10°	20°	30°
Pressure in atmospheres	35·4	44·4	56·4	70·7

The full discussion of the results is reserved for a future paper. H. C.

Heat of Formation of Platinic Bromide and its principal Compounds. By L. Pigeon (*Compt. rend.*, **113**, 476—479).—Platinic bromide, prepared by carefully heating hydrogen platinic bromide, was dissolved in water, 9·86 Cal. being developed. The solution was then reduced by metallic cobalt, the heat developed being 93·59 Cal. By subtracting the heat of formation of the cobalt bromide, 145·88 Cal., we get for the heat of formation of dissolved platinic bromide 52·29 Cal., and from this the heat of formation of the solid salt, 42·43 Cal. Solid platinic bromide dissolved in hydrobromic acid solution (1 mol. in 4 litres) gives rise to a development of 15·27 Cal., from which the heat of formation of a solution of

hydrogen platinic bromide from platinum, bromine, and hydrobromic acid is 60 70 Cal. The formation of the crystalline salt $H_2PtBr_6 + 9H_2O$ is attended by the development of an additional 2·86 Cal.

The author draws attention to the fact that the heats of formation of the compounds of platinum and bromine are, when gaseous bromine is taken, very nearly equal to the heats of formation of the similar compounds of platinum and chlorine. H. C.

Heats of Combustion and Formation of Nitrobenzenes. By Berthelot and Matignon (*Compt. rend.*, **113**, 246—249) :—

	Heat of combustion, constant volume.	Heat of combustion, constant pressure.	Formation from elements.	Formation from nitric acid.
	Cal.	Cal.	Cal.	Cal.
Orthodinitrobenzene.....	+704·6	+703 5	+0·5	+58·3
Metadinitrobenzene	+698·1	+697·0	+6·8	+64·8
Paradinitrobenzene	+696·5	+695·4	+8·4	+66·4
Trinitrobenzene (1 : 3 : 5).....	+665·9	+663·8	+5·5	+90·9
Trinitrobenzene (1 : 2 : 4).....	+680·6	+678·5	−9·2	+76·2

It is clear that although the values for the various isomerides are very similar, as is usually the case, there are distinct differences, amounting to 1 per cent. in the case of the dinitro-derivatives, and to 2 per cent. in the case of trinitro-derivatives. The differences are also distinct in the case of the formation from nitric acid, and the heat developed becomes less the more advanced the substitution.

The heat of formation of a nitro-derivative is always but slightly different from that of the generating hydrocarbon ; and it follows that the oxygen of the nitroxyl group has nearly the same combustible power as if it were in the free state. Since the heat of formation becomes less as nitration advances, it follows that the combustible energy of the oxygen gradually increases. The bearing of this result on the explosibility of nitro-derivatives is obvious.

C. H. B.

Calorific Value of Food Constituents and their Derivatives. By F. Stohmann and H. Langbein (*J. pr. Chem.* [2], **44**, 336—399). —Stohmann is surprised that Berthelot (*Ann. Chim. Phys.* [6], **22**, 5) has not quoted him as an authority on the thermochemistry of proteïds and made use of his work on the subject (compare Abstr., 1885, 857).

The authors have already dealt with the calorific values of animal fats (Abstr., 1891, 11) ; in this paper they summarise the calorific values which they obtain for various proteïds and the products of their change. Full data for the results, and details as to source of the compounds, are given. The following tables summarise the values,

	Calorific value per gram, cal.	Ultimate composition.						Atomic proportions.
		Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Chlorine.	
Elastin	5961·3	55·03	7·20	16·91	0·18	20·68	—	$C_{720}H_{1129}N_{190}SO_{202}$.
Vegetable fibrin	5941·6	54·39	6·92	15·39	1·02	22·28	—	$C_{720}H_{1100}N_{175}S_5O_{221}$.
Serum albumin	5917·8	53·93	7·65	15·15	1·18	22·09	—	$C_{720}H_{1227}N_{173}S_8O_{221}$.
Syntonin	5907·8	53·64	7·44	15·76	1·09	22·07	—	$C_{720}H_{1198}N_{182}S_5O_{222}$.
Hæmoglobin	5885·1	54·73	6·06	16·50	0·46	22·25	—	$C_{720}H_{957}N_{186}S_2O_{219}$.
Milk caseïn, No. 1	5867·0	54·02	7·33	15·52	0·75	22·38	—	$C_{720}H_{1173}N_{178}S_4O_{224}$.
„ „ No. 2	5849·6	54·14	6·85	15·61	0·78	22·62	—	$C_{720}H_{1093}N_{179}S_4O_{225}$.
Yolk of egg	5840·9	53·50	7·31	15·26	1·11	22·82	—	$C_{720}H_{1180}N_{176}S_6O_{231}$.
Legumin	5793·1	53·22	7·17	15·18	0·46	23·97	—	$C_{720}H_{1165}N_{175}S_2O_{244}$.
Vitellin	5745·1	50·27	7·90	16·04	1·09	24·70	—	$C_{720}H_{1357}N_{198}S_6O_{264}$.
Egg albumin	5735·2	52·95	7·50	15·19	1·51	22·85	—	$C_{720}H_{1224}N_{178}S_8O_{233}$.
Flesh fibre, No. 5	5720·5	52·11	7·10	16·44	1·03	23·32	—	$C_{720}H_{1178}N_{194}S_5O_{242}$.
Crystallised albumin	5672·0	51·48	6·76	18·14	0·96	22·66	—	$C_{720}H_{1134}N_{218}S_5O_{248}$.
Flesh, No. 3	5662·6	—	—	16·38	1·09	—	—	
„ No. 1	5640·9	52·02	7·30	16·36	1·01	23·31	—	$C_{720}H_{1214}N_{195}S_5O_{243}$.
Blood fibrin	5637·1	52·93	7·16	16·72	1·13	22·06	—	$C_{720}H_{1169}N_{194}S_6O_{225}$.
Harnack's albumin	5553·0	50·69	6·68	14·51	1·89	23·67	2·56	$C_{720}H_{1140}N_{177}S_{10}Cl_{11}O_{252}$.
Wool fibre	5510·2	50·20	6·72	16·54	3·70	22·84	—	$C_{720}H_{1157}N_{203}S_{20}O_{246}$.
Conglutin	5479·0	50·78	6·74	17·51	0·79	24·18	—	$C_{720}H_{1147}N_{213}S_4O_{257}$.
Skin fibroïn	5355·1	49·92	5·75	18·01	0·30	26·02	—	$C_{720}H_{995}N_{223}S_2O_{282}$.
Peptone	5298·8	50·10	6·45	16·42	1·24	25·79	—	$C_{720}H_{1111}N_{201}S_7O_{277}$.
Chondrin	5130·6	49·14	6·67	15·37	1·26	27·56	—	$C_{720}H_{1171}N_{193}S_7O_{302}$.
Osseïn	5039·9	48·63	6·64	16·34	0·95	27·44	—	$C_{720}H_{1192}N_{210}S_5O_{309}$.
Fibroïn	4979·6	48·63	6·08	18·97	—	26·32	—	$C_{720}H_{1091}N_{244}O_{294}$.
Chitin	4650·3	45·15	6·40	6·86(?)	—	41·59	—	$C_{720}H_{1225}N_{93}O_{728}$.

the atomic proportions in Table I being calculated to 720 carbon atoms to avoid decimals; 72 is the proportion of carbon atoms found in white of egg by Lieberkühn.

	Composition.	Mol. weight.	Calorific value.	Heat of formation.	Calorific value according to Berthelot.	
			Cal.	Cal.	Cal.	
Glycocine.....	$C_2H_5NO_2$	75	234·6	125·9	234·9	B and A.
Alanine.....	$C_3H_7NO_2$	89	387·7	135·8	389·0	B and A.
Leucine.....	$C_6H_{13}NO_2$	131	855·8	156·7	857·1	B and A.
Sarcosine	$C_3H_7NO_2$	89	401·2	122·3	—	
Hippuric acid...	$C_9H_9NO_3$	179	1014·5	142·0	1012·9	B and A.
Aspartic acid...	$C_4H_7NO_4$	133	385·2	232·3	386·8	B and A.
Urea	CH_4N_2O	60	152·2	79·8	151·5	B and P.
Asparagine.....	$C_4H_8N_2O_3$	132	463·5	188·5	448·1	B and A.
Kreatine (cryst.)	$C_4H_9N_3O_2,H_2O$	149	553·3	202·2	—	
Kreatine (anhydrous).....	$C_4H_9N_3O_2$	131	560·0	126·5	—	
Uric acid	$C_5H_4N_4O_3$	168	460·5	148·5	461·4	M.
Guanine.....	$C_5H_5N_5O$	151	586·6	55·9	—	
Caffeïne	$C_8H_{10}N_4O_2$	194	1014·9	82·1	—	

B and A = Berthelot and André, B and P = Berthelot and Petit, M = Matignon.

In connection with the first of these tables, the authors give another table showing the results which were obtained by Berthelot and André for some of the proteïds in the authors' table; this table appears to be quoted from *Ann. Chim. Phys.* [6], **22**, 25, which contains the same table as appears in Abstr., 1890, 937, but the numbers given here do not quite agree with those in the table referred to.

If the values for elastin, wool-fibre, skin-fibroïn, chondrin, osseïn, fibroïn, and chitin be excepted, the mean calorific value for the proteïds given in the first table is 5730·8 cal. Berthelot (Abstr., 1890, 938) found 5691 cal. for this number; the authors regard the mean, 5711 cal., as representing the real value. This value would be given by the formula $C_{720}H_{1161}N_{187}S_5O_{238}$; Lieberkühn's formula is $C_{72}H_{112}N_{18}SO_{22}$.

From the values given in the second table, the authors deduce the following generalisations:—(1) The substitution of CH_3 for a hydrogen atom in homologous series increases the calorific value by 156—157 Cal. (2) The calorific value of a methyl group attached to a nitrogen atom is higher than that of one attached to a carbon atom. (3) The displacement of a hydrogen atom in a CH_2 group by NH_2 raises the calorific value by 26·9 Cal. (4) The displacement of the hydroxyl in a carboxyl group by NH_2 raises the calorific value by 78·6 Cal. The heat of combustion of carbonic acid deduced from that of urea by means of this generalisation is −5·0 Cal. Longuinine (*Ann. Chim. Phys.* [6], **8**, 133) found −4·3 Cal. and −10·75 Cal. for this number.

A. G. B.

Maximum Density of Water. By H. M. Vernon (*Phil. Mag.* [5], **31**, 387—392).—The author investigated the rate of cooling of quantities of water from 30° down to 0°. His thermometer was read to 0·01° by means of a cathetometer. When the water was not stirred, there was a sudden break in the cooling curve about 4·7°, which is therefore to be considered the point of maximum density. No break appeared when the water was stirred, the natural convection currents not then having free play; but from the form of the curve it would seem that the specific heat of water between 0° and 12° is about 3 per cent. greater than between 16° and 30°. Both the increased specific heat and the maximum density are considered by the author to have their cause in an aggregation of $(H_2O)_2$ molecules to $(H_2O)_4$ molecules about 4° as the water cools. J. W.

Expansion of Water. By C. Scheel (*Chem. Centr.*, 1891, ii, 409—410; *Inaug. Diss., Berlin*).—The author has determined the expansion of water between 0° and 33° by means of a glass apparatus, the volume being read off on a capillary tube. (For a complete description of it, see the original paper.) The absolute expansion of water was found to be 0·0408059, the minimum being at 4·058°.

J. W. L.

Dilatation of Phosphorus and its Change of Volume at the Melting Point. By A. Leduc (*Compt. rend.*, **113**, 259—261).—Phosphorus expands almost regularly up to its melting point, which is 44·2° on the mercurial thermometer, and 44·1° on the normal thermometer. At this point, without any appreciable change of temperature, there is a considerable expansion, the ratio of the volume of the solid phosphorus to that of the liquid phosphorus being 1 : 1·0345. Kopp's number was 1·0343.

The expansion of either solid or liquid phosphorus can only be represented by a formula with three terms, but the author is not able to state the coefficients precisely. The value of the mean coefficients on the normal thermometer between 0° and 44·1° is 0·000372, and between 26° and 50°, 0·000560, the latter being calculated on the volume at 0°. These values differ considerably from those given by Kopp. C. H. B.

Capillary Constants of Salts at their Melting Points. By J. Traube (*Ber.*, **24**, 3074—3080).—The author has determined the capillary constants of a large number of salts at temperatures just above their melting points. The method adopted was that of weighing the drops which fell from a single perforation in a small disc that formed the end surface of a short cylinder let in to the bottom of a platinum or porcelain crucible. This crucible was so heated, by means of an ordinary gas flame or by the blowpipe, that the flame did not come in contact with the hanging drop. The salts investigated were potassium and sodium salts, and the ratios (T) of the weight of the drops to the weight of the water-drop at 0° from the same vessel are tabulated.

From his results, the author deduces the following conclusions:—Capillarity may be considered a "colligative" property. The con-

stants for the salts of the fatty acids are unusually small, diminishing rapidly as the series is ascended. For the other salts the constants (T) of the potassium salts of monobasic acids lie between 112 and 157; of bibasic and multibasic acids, between 168 and 231. The limits for the constants of the corresponding sodium salts are 123—161, and 189—325. The difference $T_{Na} - T_K$ increases with the number of equivalents of the metal in the salts. It is doubtful if tri- and quadri-basic acids can, in this way, be distinguished from bibasic acids, but the author considers it always possible to distinguish between the latter and monobasic acids. The method points to the following formulæ as being correct :—K_2F_2, $K_2P_2O_6$, $Na_2P_2O_6$, $K_2As_2O_6$. J. W.

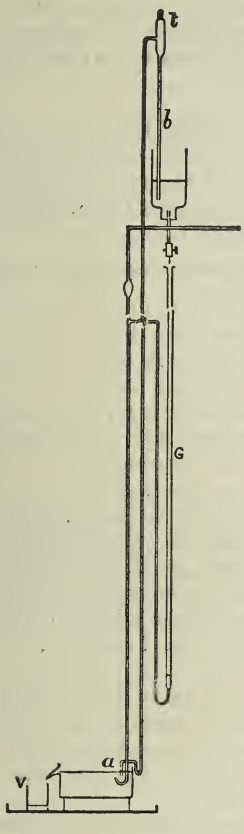
Mutual Solubility of Salts in Water. By W. W. J. Nicol (*Phil. Mag.* [5], **31**, 369—387).—Under the heading "The Mutual Solubility of Salts," the author groups the phenomena due to the mutual influence of two salts on each other's solubility in water. He gives an historical survey of the work done on the subject, and proceeds to communicate his own experiments on the chlorides and nitrates of sodium and potassium taken in all possible combinations of pairs with a common constituent. The method of experiment adopted was as follows:—A salt was taken, and solutions containing 1, 2, &c., gram-mols. of this salt in 100 gram-mols. of water were prepared. These solutions were then saturated at a definite temperature with the other salt added in excess, and the total salt in solution determined. Precisely similar determinations were made with definite molecular solutions of the other salt. The solubility of each salt separately in water was then determined, and finally, the solubility of both salts when simultaneously added in excess to water was also ascertained.

The results are presented in the form of tables, formulæ, and curves. In general, the presence of one salt diminishes the solubility of the other, but in the case of the nitrates of potassium and sodium, the presence of the one in solution increases the solubility of the other. (Compare Nernst, Abstr., 1890, 3; Le Blanc and Noyes, Abstr., 1891, 388.) J. W.

Cryoscopic Behaviour of Dilute Solutions. By J. Traube (*Ber.*, **24**, 3071—3074).—Eykmann and Arrhenius have pointed out (Abstr., 1891, 972 and 1148) that the observations of the author on the freezing point of dilute solutions, in particular of those of cane sugar, are not in accordance with their own experiments, or with those of Tammann and Pickering. The author upholds his numbers, and attributes the discrepancy to the other observers having cooled their solutions too far below the freezing point before making observations. J. W.

Automatic Replacement of Mercury in Sprengel Pumps. By A. Verneuil (*Bull. Soc. Chim.* [3], **5**, 748—750).—The mercury is continuously and automatically transferred from the lower to the upper reservoir by the action of a water-pressure or similar pump,

the suction-tube of which is attached to the upper end *t* of a small bulb, connected by tubes *a*, *b* to both reservoirs, and placed about 40 cm. above the upper one. The contents of the lower reservoir are thus forced into the bulb by atmospheric pressure, and allowed to



fall into the upper reservoir by their own weight. The tube *a* is 3 mm. in internal diameter, and is recurved at the lower end, the level of the mercury at that point being so adjusted that much air and little mercury passes up the tube; the tube *b* is 6 mm. in internal diameter.

The apparatus is applicable to most existing mercury pumps. It is not intended to be used at starting, as it is found more convenient to transfer any considerable quantity of mercury by hand than to make the apparatus of unnecessarily large dimensions. An incidental advantage is that the mercury is brought into contact with air under conditions favourable to the oxidation of impurities.

Jn. W.

Block Support for Tubes. By A. Gawalovski (*Zeit. anal. Chem.*, **30**, 581—583).—Two elongated blocks of hard wood, laid side

by side, have rectangular grooves ploughed in their contiguous faces, so as to form a channel, the cross section of which corresponds, approximately, with the shape of the bulbs of a Péligot's U-tube. The blocks are then united by screws. Upright pieces of wood, of various heights, shaped so as to fit and slide in the channels, can be inserted to give support to the U-tubes, or to carry horizontal tubes on their upper, grooved edges. To these pieces the tubes are attached by spring clips. A train of tube apparatus can thus be held by a single support. M. J. S.

Formation of Mixed Crystals. By H. Behrens (*Rec. Trav. Chim.*, **10**, 57—64).—1. *Double Salts of Mercuric Thiocyanate with Zinc, Cadmium, Cobalt, and Copper Thiocyanates.*—The salts having the following compositions, crystallise well :—$Hg(CNS)_2,Zn(CNS)_2$; $Hg(CNS)_2,Co(CNS)_2$; $2Hg(CNS)_2,Cd(CNS)_2$; and

$$Hg(CNS)_2,Cu(CNS)_2 + H_2O.$$

The zinc and cobalt double salts are homogeneous crystals, the former colourless, and the latter deep-blue. The cadmium salts afford analogous, pale-blue crystals, which, in the case of the double salts of zinc and cadmium, are almost identical in form with those of zinc mercury thiocyanate; consequently, two double cadmium mercury thiocyanates should exist and correspond with the formulæ $2Hg(CNS)_2,Cd(CNS)_2$ (Nordström's salt) and $Hg(CNS_2),Cd(CNS)_2$ respectively, which are analogous to the ammonium salts $Hg(CNS)_2,NH_4CNS$ and $Hg(CNS)_2,2NH_4CNS$.

From the liquid obtained by the addition of mixed solutions of cobalt and cadmium nitrates, or of cobalt and zinc nitrates, to a very dilute solution of ammonium mercury thiocyanate, colourless needles separate; these break up on the addition of ammonium thiocyanate, when the mother liquor affords the large, mixed, deep-blue crystals, noted above.

No mixed crystals of cobalt and copper compounds could be obtained. With the blue crystals of the cobalt salt, yellowish-green crystals of mercury copper thiocyanate occur, a result the author ascribes to a reaction induced by the water of crystallisation the double copper salt contains.

Addition of mercury ammonium thiocyanate to mixed solutions of copper, zinc, cobalt, and cadmium salts, determines the formation of mercury copper thiocyanate, and characteristic brown-violet crystals of mercury zinc copper thiocyanate, which contain no cobalt, and are isomorphous with the zinc compound. These do not alter when heated at 120°, whereas the dark-green needles of mercury copper thiocyanate become dark and opaque. The author concludes that, in presence of much zinc, mercury copper thiocyanate loses its water of crystallisation yielding mixed crystals with mercury zinc thiocyanate, whereas when mercury copper thiocyanate crystallises alone, it always contains a molecule of water of crystallisation.

2. *Silver Chromate and Silver Sulphate.*—The small, red crystals, forming the precipitate produced by the addition of potassium dichromate solution to a silver nitrate solution acidified with nitric

acid belong, like potassium dichromate, to the clinorhombic system. If silver sulphate be substituted for silver nitrate, the blood-red crystals yielded at first are monoclinic, but are succeeded by the deposition of orange-yellow, orthorhombic crystals of the mixed salt $Ag_2SO_4 + Ag_2CrO_4$, with liberation of chromic acid.

3. *Phosphates and Arsenates of the type* $NH_4MgPO_4 + 6H_2O$.—Salts of this type form hemimorphic orthorhombs. The corresponding hemimorphic double phosphates of magnesium, manganese, cobalt, and nickel are known, and the author has prepared the analogous arsenates of calcium, zinc, and copper. He describes and figures crystals obtained by him in endeavouring to produce mixed crystals of these salts, in order to determine if their constitution was of the same type as the magnesium derivative. Although in this respect his results are not conclusive, yet from the development of the crystals he concludes that neither a central point nor a plane of symmetry is necessary to the development of hemimorphic crystals, since they originate equally well from a lateral plane or a summit.

T. G. N.

Inorganic Chemistry.

Revised Hydrochloric Acid Tables. By G. Lunge and L. Marchlewski (*Zeit. ang. Chem.*, 1891, 133—135).—The authors have constructed a very useful table, giving the specific gravities (reduced by Kohlrausch's formula to vacuum and 4° C.), the corresponding degrees of Baume's and Twaddell's hydrometers, the percentage of hydrogen chloride by weight, the percentage of weight of 18°, 19°, 20°, 21°, and 22° acid, and the number of kilograms of the said acids contained in 1 litre. The specific gravities were taken with the utmost care in a specific gravity bottle, provided with an accurate thermometer, and are guaranteed to be accurate within 0·0001. The acid was analysed by titration with N/5 solution of sodium hydroxide, which had been standardised with N/5 hydrochloric acid. This acid was standardised with pure sodium carbonate, and the results were verified by a gravimetric estimation as silver chloride. The titrations were done with the greatest care, and the experimental error never exceeded 0·02 per cent. with the weaker acids, and 0·05 per cent. with the stronger ones. The weaker acids were weighed in a Winkler's stop-cock pipette; the fuming ones in sealed glass bulbs.

L. de K.

The Place of Fluorine in the Classification of the Elements. By H. Moissan (*Bull. Soc. Chim.* [3], **5**, 880—885).—Whilst fluorine in many respects behaves as the most energetic member of the chlorine family, in some ways it is markedly distinguished from chlorine, and seems almost to bear a remote analogy to oxygen; as instances in point are cited, the ready combustibility of charcoal in fluorine, the dissimilarity of calcium fluoride from the chloride, and its

resemblance to the oxide, the solubility of silver fluoride in water, and the stability of aluminium fluoride towards water. It is pointed out also that, whilst the compounds of fluorine with the non-metallic elements, including its organic compounds, are uniformly more volatile than the corresponding compounds of chlorine, its metallic salts require, as a rule, a higher temperature for fusion than the corresponding chlorides. Comparative numerical data are given.

Jn. W.

Action of Fluorine on Phosphorus Trifluoride. By H. Moissan (*Bull. Soc. Chim.* [3], **5**, 880).—In order to study the action of fluorine on other gaseous substances, the two gases were admitted by separate tubes to the central portion of a platinum tube 15 cm. long, the ends of which were closed by transparent plates of fluorspar, and the resulting gaseous product was conducted to the water or mercury trough by a third tube near the end. When fluorine comes in contact with phosphorus trifluoride, a yellow flame of low temperature is seen, and the product of the reaction is mainly phosphorus pentafluoride, the residue consisting of unchanged trifluoride. Jn. W.

Persulphates. By Berthelot (*Compt. rend.*, **112**, 1481—1483; see also Berthelot, *Compt. rend.*, **86**, 20, 71, and 277; Marshall, Trans., 1891, 771; Mendeléeff, *Bull. Soc. Chim.*, **38**, 168; Traube, *Ber.*, **22**, 1518, and **24**, 1764).—The mixture of persulphuric and sulphuric acids obtained by electrolysis, when neutralised by baryta-water or potash solution, yields a quantity of the normal persulphate, which is greater when the operation is carried on at a very low temperature. The neutralised solution rapidly becomes acid again, particularly on heating; at the same time losing oxygen. The quantity of active oxygen is proportional to the quantity of sulphuric acid formed in the decomposition.

Barium persulphate is soluble, and as neutral as the thiosulphate or permanganate; its decomposition proceeds according to the equation $BaS_2O_8 + H_2O = BaSO_4 + H_2SO_4 + O$.

In titrating the active oxygen by the usual reagents, it is necessary to take into account the hydrogen peroxide often coexistent with persulphuric acid, or capable of being formed during the dilutions and other operations. The proportion of hydrogen peroxide present has been found to vary from 0 to 2 mols. for each mol. of persulphuric acid. Viewing the whole of the active oxygen present in the extreme case as united to the sulphur, the complex acid would have the formula S_2O_9,nH_2O. There is no proof of the existence of a neutral and anhydrous compound, such as the holoxide, SO_4, of Traube.

The salts of persulphuric acid are distinct and definite, and comparable with the permanganates, perchlorates, permolybdates, and pertungstates. W. T.

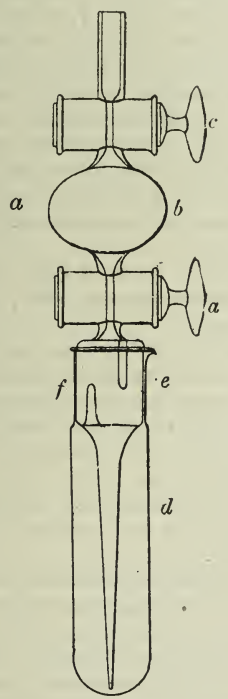
Thiosulphates. By A. Fock and K. Klüss (*Ber.*, **24**, 3016—3017). —*Potassium calcium thiosulphate*, $3K_2S_2O_3,CaS_2O_3 + 5H_2O$, is obtained in colourless, monosymmetric crystals, by evaporating on the water-bath a mixture of potassium and calcium thiosulphate solutions.

The axial relation of the crystals is $a : b : c = 1{\cdot}7010 : 1 : 0{\cdot}8931$; $\beta = 80° 2'$.

Potassium strontium thiosulphate, $K_2S_2O_3,SrS_2O_3 + 5H_2O$, is prepared in a similar manner to the calcium salt; it is readily soluble in water, and crystallises in slender, lustrous, silky needles, which are not well adapted for crystallographic measurements. J. B. T.

Ammonium Dithionate Hydrochloride. By A. Fock and K. Klüss (*Ber.*, **24**, 3017—3018).—On mixing solutions of ammonium dithionate and ammonium chloride in molecular proportions, and evaporating, a compound of the formula $(NH_4)_2S_2O_6,HCl$, is deposited in rhombic crystals. The axial relation is $a : b : c = 0{\cdot}09827 : 1 : 0{\cdot}9612$. The same substance is also formed in presence of two or more molecular proportions of ammonium chloride. J. B. T.

Revised Nitric Acid Tables. By G. Lunge and H. Rey (*Zeit. ang. Chem.*, 1891, 165—170).—The tables are constructed on similar lines to the revised hydrochloric acid tables (compare this vol., p. 11), and similar processes were employed in their construction, but instead of weighing the acid in glass bulbs, or in a Winkler's stop-



cock pipette, a new form of weighing pipette, shown in the figure, was used.

Above the stop-cock *a* is fixed a bulb *b*, of about 2 cm. diameter, connected with a second stop-cock *c*. The lower part of the pipette fits into a glass tube *d*, which has a ground neck. When the pipette is wanted for use, the stop-cock *a* is closed; suction with the mouth is applied to the top, and the stop-cock *c* immediately closed, by which means a diminished pressure will be obtained inside the bulb *b*. The point of the pipette is now dipped into the acid, the stop-cock *a* opened, and the acid allowed to ascend as far as the stop-cock, which is then immediately turned off. After wiping the pipette, it is fixed into the tube *d* and weighed. The pipette is now turned round, so as to open communication between the channels *e* and *f*. The stop-cock *c* is opened, water is squirted into the bulb *b*, and then allowed to flow through *a* into the pipette. The diluted acid runs into the tube *d*, the air of which escapes through *e* and *f*. The acid is finally emptied into a beaker and titrated. By using this apparatus, any loss of nitric fumes is avoided. L. DE K.

Compounds of Sulphur and Phosphorus. By J. MAI (*Annalen*, **265**, 192—208).—The object of these experiments was to ascertain whether the boiling point of triphosphorus hexasulphide, P_3S_6, was sufficiently below that of stannous chloride (606°), and above that of phosphorus pentasulphide (518°), to allow of its advantageous employment as a heating vapour in pyrochemical investigations.

When an intimate mixture of sulphur (2 atoms) and amorphous phosphorus (1 atom) is carefully heated in an atmosphere of carbonic anhydride, and the product then distilled, a yellow, crystalline substance (b. p. about 410°), which seems to contain the compound P_4S_3, passes over first; the later fractions consist of a mixture of triphosphorus hexasulphide and phosphorus pentasulphide, which cannot be separated into its constituents, as they boil at the same temperature (about 508°).

Phosphorus pentasulphide boils at 332—340° under a pressure of 10—11 mm.; triphosphorus hexasulphide, P_3S_6, boils at 335—340° under the same conditions.

When the compound of the composition P_4S_3, prepared from its elements by the usual method, is distilled under a pressure of 11 mm., a yellow liquid passes over between 230° and 240°, and amorphous phosphorus remains in the flask; the distillate is almost completely soluble in carbon bisulphide, from which it is gradually deposited in crystals of the composition P_4S_3. The boiling point of this compound under the ordinary pressure would be about 408—418°; it begins to soften at 130—135°, but does not melt completely until the temperature has risen above 160°.

When phosphorus (2 atoms) is melted with sulphur (3 atoms), and the product submitted to distillation under a pressure of 11 mm., almost the whole passes over between 285° and 335°; the distillate slowly solidifies to a yellowish, resinous, pasty mass, which, when digested with carbon bisulphide under pressure, yields a crystalline compound of the composition P_4S_7; the mother liquors from this compound contain a crystalline substance, which seems to be a mixture of phosphorus trisulphide with P_4S_5. F. S. K.

New Method of Preparing Carbon Oxysulphide. By J. Nuricsán (*Ber.*, **24**, 2967—2974).—Carbon oxysulphide is obtained when carbonyl chloride is passed through concentrated sulphuric acid to dry it, and then through a tube 50 cm. long, filled with ignited asbestos well mixed with finely pulverised cadmium sulphide, the tube being placed in a combustion furnace and heated. The author finds that even when no external heat is applied a small quantity of carbonyl sulphide is formed, but the most favourable temperature for its formation appears to be 260—280°. The gas thus produced was found on analysis to contain COS, 94·87 per cent.; CO, 3·98 per cent.; air, 1·15 per cent. A quantity of crystals, which were identified as cadmium chloride, were observed in a tube previously charged with a layer of cadmium sulphide and heated in a flame during the passage of a current of carbonyl chloride; the reaction, therefore, appears to be a double decomposition.

A. R. L.

Allotropic Silver. III. Blue Silver. By M. C. Lea (*Phil. Mag.* [5], **31**, 497—504; compare Abstr., 1891, 803).—When silver nitrate is added to a solution of dextrin made alkaline with sodium or potassium hydroxide, the alkali being kept in moderate excess, the silver is first precipitated as the ordinary brown oxide, but the colour gradually changes to reddish-chocolate, and the silver begins to dissolve, and in a few minutes has completely dissolved to form an almost black liquid, a few drops of which, when added to a large quantity of water, give a splendid red liquid, that spectroscopic examination shows to be a perfect solution. Different specimens of dextrin behave differently, and the common brown form seems to give the best results. Convenient proportions are 20 grams of sodium hydroxide and 20 grams of dextrin in 1000 c.c. of water, 14 grams of silver nitrate previously dissolved in a small quantity of water being gradually added.

It is interesting to observe that allotropic silver can be formed and can exist in solution in neutral, acid, and alkaline liquids. The alkaline solution spontaneously deposits allotropic silver after some time, and precipitation is immediate on the addition of dilute nitric or sulphuric acid. Even with a large excess of acetic acid, however, precipitation is incomplete. When the precipitate has once formed, it is almost insoluble, but on washing dissolves to a very small extent, forming a rose-red liquid.

A small quantity of sodium phosphate, when added to the alkaline solution, precipitates the whole of the allotropic silver with a ruby-copper colour, which after prolonged washing changes to deep Nile-green, and becomes slightly soluble, forming a wine-red solution.

The various forms of allotropic silver show different body and surface colours, which tend to be complementary. The precipitate by sodium phosphate, for example, when spread thickly on paper, dries with a bright-green, metallic colour, but after it has been changed to deep green by washing, films dry with a dark gold or copper surface-colour.

Although the dry substance has all the appearance of a metal, it

may contain 8 to 10 per cent. of organic matter that cannot be removed, even by prolonged washing with hot water under pressure. Four specimens of carefully purified material contained respectively 93·77, 94·27, 92·86, and 96·64 per cent. of metallic silver. When the allotropic forms are heated, a vapour is evolved which condenses in small, brownish drops, with an empyreumatic odour. The residue consists of bright white metallic silver, and when dissolved in nitric acid, leaves a residue of black flakes of carbon. When the allotropic silver is dissolved in dilute nitric acid, and the silver precipitated by hydrochloric acid, the filtrate, on evaporation, leaves a small residue of a yellowish, gummy substance.

Tannin reduces silver nitrate to allotropic silver more readily than does dextrin, and gives better results in presence of sodium or potassium carbonate than with the caustic alkalis. 24 grams of anhydrous sodium carbonate are dissolved in 1200 c.c. of water, and mixed with 72 c.c. of a filtered 4 per cent. solution of tannin. 24 grams of silver nitrate dissolved in a small quantity of water is added gradually, and solution of the silver takes place immediately. After standing for a day or two, the intensely dark-coloured liquid may be poured off from a small quantity of black precipitate. On adding a small quantity of dilute acid, the allotropic silver is precipitated, and in films dries with a bluish, steel-grey, surface-colour.

Blue allotropic silver (including the green and steel-grey varieties) shows endless variations, and cannot be reduced to one type. Slight differences in the conditions of formation result in very different products. Of ten products obtained by the action of tannin and sodium carbonate in various proportions, several were easily and completely soluble in ammonia, whilst some dissolved slightly, and others not at all. Some of the specimens, insoluble in water, when treated with phosphoric acid, did not dissolve, but on washing away the acid, were found to have become soluble in water; other insoluble specimens did not behave in this way. Some of the solutions were scarcely affected by acetic acid, whilst others were partially, and others almost completely, precipitated.

The films on paper vary greatly in their sensitiveness to light, and in the ease with which they are converted into the yellow, intermediate form. The least sensitive modification is that precipitated by nitric acid; it dries with a steel-grey colour. The modifications precipitated by acetic acid tend to have a greenish metallic surface, and are more sensitive. Permanency varies greatly in different specimens, and is increased by thorough washing.

The blue, grey, and green forms are related to the black, or dark-grey normal silver, and tend to pass into it, whilst the gold-coloured modification tends to change into bright white metallic silver on the surface, with dark, or even black, silver underneath.

Tannin likewise reduces silver nitrate in presence of lithium, ammonium, magnesium, barium, calcium, and strontium carbonates. The product with strontium carbonate is dark-red whilst moist, but dries with a rich, bluish-green, metallic surface-colour in thick films, but is red and transparent in thin films.

The intermediate golden-yellow form produced during the passage of the gold-coloured allotropic form to white normal silver has none of the properties of the original form, except its colour and lustre. It is hard and tough, is not converted into normal silver by friction and high pressure, and offers as much resistance as normal silver to the action of oxidising and chlorinating agents. The difference between the original form and the intermediate form lies in the fact that the latter has a crystalline structure, which becomes evident on treating the film with ferric chloride solution.

When the blue form is gently heated, it also first becomes yellow, and then changes to white normal silver. A film on glass begins to change from blue to yellow at about 180°, and the same change is produced by the action of light, some specimens requiring a few hours' exposure to sunlight, whilst others require several days.

The author considers that in these allotropic forms the silver exists in a state of atomic division, and that this is true also of the pyrophoric forms of various metals. He points out that there is a difference between chemical and mechanical division, and that a metal may form a compact mass, and yet be in a state of atomic division, whilst on the other hand it may be in a fine state of mechanical division, and yet possess a high degree of molecular complexity. C. H. B.

Characteristics of the Alkaline Earths. By G. Brügelmann (*Zeit. anal. Chem.*, **30**, 579—580).—In his attempts to prepare baryta by igniting the hydroxide in graphite crucibles, the author has been unable to obtain a pure product, the crucible being always attacked. The supposition of the dimorphism of barium oxide, and the assumed catalytic action of platinum (Abstr., 1890, 850), must therefore be abandoned, since the substance obtained as a felted mass of needles showing chromatic polarisation can no longer be regarded as baryta. Since a similar action occurs with lime and strontia, all statements respecting the specific gravity, &c., of the alkaline earths prepared in other than platinum vessels, must be withdrawn. The statements of Fresenius and others, that strontium carbonate fuses while decomposing, cannot be confirmed. Much contraction occurs, but the oxide produced retains the form of the original mass of carbonate, and is, at most, slightly sintered. M. J. S.

Composition of a Boiler Incrustation. By A. Christ (*Zeit. ang. Chem.*, 1891, 77).—The author communicates an analysis of a curious boiler deposit, which owed its origin partly to the use of an animal or a vegetable lubricating oil. CaO, 11·09; MgO, 9·79; Fe_2O_3, 5·60; Al_2O_3, 1·10; PbO, 0·98; CuO, trace; SiO_2, 16·00; SO_3, 1·71; fatty acids, 22·62; neutral fats, 23·84; moisture, 2·69; combined water and organic matter, 5·22 per cent. L. de K.

Action of Hydrogen Peroxide and of Water saturated with Carbonic Anhydride on Magnesium. By G. Giorgis (*Gazzetta*, **21**, 510—514).—According to Weltzien (*Annalen*, **138**, 132), hydrogen peroxide acts slowly on magnesium, forming an alkaline liquid, which contains the normal hydroxide, $Mg(OH)_2$, and on evaporation to dry-

ness leaves a white, strongly alkaline mass, completely soluble in water. The author has also observed the slow action of hydrogen peroxide on magnesium and the alkalinity of the solution, but finds that, after remaining for a few days, acicular crystals are deposited, which effervesce on treatment with hydrochloric acid. On treating metallic magnesium in a vacuum with hydrogen peroxide free from carbonic anhydride, the liquid after a time becomes slightly alkaline, and on evaporating to dryness in a vacuum, a flocculent precipitate separates, which is only very sparingly soluble in water free from carbonic anhydride. On the other hand, when magnesium is treated with distilled water saturated with pure carbonic anhydride, the liquid soon becomes strongly alkaline, and the metal is energetically attacked with evolution of hydrogen; the reaction slackens very gradually, and gas ceases to come off after about 10 or 12 hours. The solution, after a time, deposits acicular crystals having the composition $MgCO_3 + 3H_2O$.

The evolution of hydrogen by the action of an aqueous solution of carbonic anhydride on magnesium is noteworthy; the reaction also provides an easy method for the preparation of the normal carbonate of magnesium. S. B. A. A.

Cuprammonium Oxide. By Prud'homme (*Chem. Centr.*, 1891, ii, 339—340; from *Mon. Sci.* [4], **5**, 681).—Cuprammonium oxide is a more powerful oxidising agent than hydrogen peroxide; it acts more rapidly on cellulose, and converts it into oxycellulose; it also decolorises indigo-blue more rapidly than hydrogen peroxide. With "mercerised" cotton wool, it acts like hydrogen peroxide.

In preparing it, by agitating copper turnings with ammonia and air, both cupric oxide and nitrous anhydride are formed: the nitrous anhydride is, however, only formed at a later stage of the reaction. Ammonium nitrite oxidises copper, and nitric peroxide is formed in the first instance; ammonia is also liberated by the reaction, and when this occurs, free nitrogen is formed instead of nitric peroxide. The liquid becomes intensely blue; an excess of water precipitates cupric hydroxide; dilute acetic acid precipitates cupric oxide as soon as the ammonia is exactly neutralised. J. W. L.

Action of Ferric Chloride on Metallic Sulphides. By Cammerer (*Chem. Centr.*, 1891, ii, 370; from *Berg. Hütten Zeit.*, **50**, 261—264, 282—284).—In a sealed tube, ferric chloride reacts with both cupric and cuprous sulphides, cupric chloride, ferrous chloride, and sulphur being formed. With precipitated ferrous sulphide or iron pyrites, ferrous chloride and sulphur are the products; with copper pyrites, cupric chloride, ferrous chloride, and sulphur are formed. With arsenious sulphide, ferrous chloride, sulphur, and arsenious chloride are first formed; the latter, however, is further oxidised to arsenic anhydride by the continued action of excess of ferric chloride. With either precipitated or native antimony trisulphide, antimonious chloride, ferrous chloride, and sulphur are formed. With stannous sulphide, stannic chloride, ferrous chloride, and sulphur are formed.

J. W. L.

Manganese Tetrachloride. By H. M. Vernon (*Phil. Mag.* [5], **31**, 469—484).—Fisher (Trans., 1878, 409) endeavoured to show that the dark-brown liquid obtained on dissolving manganese dioxide in hydrochloric acid contains manganese tetrachloride. Pickering, who repeated Fisher's experiments, and made, in addition, a number of his own (Trans., 1879, 654), thought that the evidence was in favour of the existence of Mn_2Cl_6 in the solution, and not of $MnCl_4$.

The author now attempts to decide between these views by experiments on the rate at which the "available" chlorine is evolved at different temperatures. If Mn_2Cl_6 is really formed in the solution, half the available chlorine should be much more easily removed by means of a current of air passed through the solution than the other half, whereas, if $MnCl_4$ is present, the rate of removal should be more regular. The curves obtained from the experimental results at various temperatures show no break at the point where half the available chlorine has been driven out, so the author concludes that when Mn_3O_4, Mn_2O_3, or MnO_2 is dissolved in hydrochloric acid, the only higher chloride formed is $MnCl_4$. The brown solution is much more stable at $-26°$ than at ordinary temperatures.

Pickering found that the presence of $MnCl_2$ in the solution from the beginning rendered it more stable. This the author accounts for on the supposition that the $MnCl_4$ dissociates directly into $MnCl_2$ and Cl_2, so that the presence in excess of $MnCl_2$, one of the products of dissociation, would diminish the actual amount of dissociation.

J. W.

Calorimetric Researches on the Condition of Silicon and of Aluminium in Cast Iron. By F. Osmond (*Compt. rend.*, **113**, 474—476).—The heat developed on dissolving 1 gram of cast iron containing different amounts of silicon in a saturated solution of the double chloride of copper and ammonium was measured. From the results, it appears that when the silicon is present in sufficient quantity, it combines with the iron with the development of heat and formation of a compound which is dissociated by an excess of iron, and therefore only exists when the amount of silicon in the alloy is sufficiently great. Hence the difference between the quantities of heat found and those calculated in the above experiments changes sign when the amount of silicon present reaches a percentage somewhere between 4·1 and 7·3.

Samples of cast iron containing aluminium were also examined in the above manner. The results show that aluminium dissolves in cast iron with the absorption of heat. H. C.

Attempts to Prepare Metallic Chromium from Chromic Fluoride. By W. P. Evans (*Zeit. ang. Chem.*, 1891, 18—20).—The author tried the effect of metallic sodium, metallic zinc, and mixed carbon and silica on chromic fluoride at a very high temperature, in the hope of getting metallic chromium.

1. Action of Sodium.—The metal was heated at 400° in a porcelain tube, and the fluoride passed over it. The latter was prepared by distilling a mixture of lead chromate, calcium fluoride, and sulphuric acid. A very strong reaction took place and the tube became

red-hot, but was soon stopped up. After cooling, the excess of sodium was dissolved out by water, and the residue examined for metallic chromium. But very little was found, and this was chiefly in combination with silicon. The experiment was repeated in an iron apparatus, in which the vapour of about 70 grams of metallic sodium was brought in contact, at a temperature of 900—1000°, with the fluoride. The chief products obtained were amorphous, green chromic oxide, bright-green particles of sodium-chromic fluoride, and a greyish, brittle, spongy mass, which was chiefly located near the fluoride delivery tube. On analysis, it proved to be an alloy of sodium with about 25 per cent. of chromium intermixed with a little chromic oxide and a trace of iron. The experiment was repeated, and, this time, to avoid contamination with iron, in a Hessian crucible. The crucible and the delivery tubes were well lined inside with a mixture of 6 parts of alumina and 1 part of potassium chloride. After being kept red-hot for half an hour, the experiment came to a premature end through the tube getting stopped up. After cooling, there was found adhering to the tube a greyish, stalactitic mass, which for the greater part dissolved in hot water. The insoluble portion consisted of fairly pure, crystalline, metallic chromium.

2. Action of Zinc.—About 200 grams of zinc was heated to boiling under a layer of salt, and the fluoride was passed in through a porcelain delivery tube. The greater part of the fluoride was taken up by the salt with formation of sodium chromate. The zinc regulus dissolved slowly in nitric acid, which gradually acquired a greenish tinge. No chromium could be detected in the insoluble residue. There was, however, good reason to believe that an alloy of zinc with about 0·67—1·80 per cent. of chromium had been formed. In the porcelain tube, however, a lustrous, steel-like substance was found, which on analysis proved to be practically pure metallic chromium.

3. Action of Carbon and Silica.—The fluoride was passed through a strongly heated porcelain tube containing small granules of a mixture of 9 parts of amorphous silica and 4 parts of powdered charcoal. Abundant vapours of silicon fluoride made their escape, and on opening the tube, sharp, shining, hexagonal crystals of chromic oxide were found; besides this, an almost black, brittle mass, which on analysis yielded Cr, 30·13; SiO_2, 48·53; C, 11·39; O, 9·95, containing, therefore, 8·39 per cent. of metallic chromium.

From these experiments, it seems that although there is not the slightest doubt about the reduction of the chromic fluoride by the processes described, it is not possible to prepare the metal on the large scale in this way. L. DE K.

Pure Bismuth. By A. CLASSEN (*J. pr. Chem.* [2], **44**, 411—414; compare Abstr., 1891, 271, 525, 1324).—This is another chapter in the controversy between Schneider and Classen as to pure bismuth. Against Schneider's analyses of commercially pure bismuth (Abstr., 1891, 1324), the author puts in two analyses, the one of "chemically pure bismuth for scientific investigations," which gave some 10 grams of lead chloride from 500 grams of the metal, the other of "bismuth

purissimum," from the same factory, which contained, besides lead (undetermined), 1·56 per cent. of copper and 0·45 per cent. of iron.

The author's electrolytic bismuth melts at 264°; "bismuth puriss." from Tromsdorff melted at 271·8°, and another sample at 273°; "absolutely pure bismuth" from Tromsdorff melted at 265—266°; "bismuth puriss." from Schering melted at 269—270°. This is further evidence of the impurity of commercial "pure bismuth."

The rest of the paper deals with Marignac's method and material, and is purely polemical. A. G. B.

Mineralogical Chemistry.

Asphalt in Utah and Colorado. By G. H. Stone (*Amer. J. Sci.*, **42**, 148—159).—In western Colorado and north-eastern Utah, asphalt deposits of four classes are represented: (1) asphaltic sand-rock, known also as sand-asphalt and bituminous rock, the most abundant of all the asphaltic deposits; (2) bituminous shales or marls; (3) bituminous limestones; and (4) outflow or overflow asphalt, including all forms of asphalt that have oozed out of the rock that originally contained them. These deposits are described in detail by the author, and the various theories that have been propounded to explain the origin of petroleum and asphalt are fully discussed. The author intends to complete a map of the asphalt exposures, and to publish a more complete account of them. B. H. B.

Gmelinite from Nova Scotia. By L. V. Pirsson (*Amer. J. Sci.*, **42**, 57—63).—The zeolites of Nova Scotia have long been noted for the size and perfection of their crystals, and amongst them gmelinite has held a prominent place. The author has consequently made a careful investigation of the crystalline form and physical properties of this mineral. The material employed was collected at Pinnacle Island, Nova Scotia. In order to control the crystallographic work, two analyses were made. In I the outer shell was analysed, and in II the inner nucleus, the results being as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
I.	50·35	18·33	0·26	1·01	0·15	9·76	20·23	100·09
II.	50·67	18·50	0·15	1·05	0·16	9·88	20·15	100·56

In considering the bearing of these results on the identity of this mineral with chabazite, there is an apparent discordance. The results of the crystallographic work point to a difference in axial ratios, and there is also a different habit and cleavage. On the other hand, the twinning and the chemical constitution indicate the identity of the species. These apparent discrepancies the author explains by the hypothesis that the effect of soda is to lengthen the vertical axis; the analyses of chabazite and gmelinite showing that soda and lime may

replace each other to any extent. According to this view, gmelinite would bear much the same relation to chabazite as enstatite does to hypersthene. Whether it should be considered a distinct species would be largely a matter of choice or convenience. B. H. B.

Newtonite and Rectorite, two new Minerals of the Kaolin Group. By R N. Brackett and J. F. Williams (*Amer. J. Sci.*, **42**, 11—21).—The authors describe two hydrous silicates of aluminium which they believe have not before been observed. The mineral, which they term *newtonite*, is found on Sneed's Creek, Newton Co., Arkansas, in a dark-grey clay, of lower carboniferous age. It is a pure white, soft, compact, homogeneous substance, having a sp. gr. of 2·37. Analysis gave the following results :—

SiO_2.	Al_2O_3.	Loss on ignition.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	Total.
40·22	35·27	22·89	0·21	0·54	0·99	0·73	100·85

These results are in accord with the formula $Al_2O_3,2SiO_2,4H_2O$. Under the microscope, the mineral is seen to be entirely made up of minute rhombs.

The second hydrous silicate of aluminium, *rectorite*, which is also to be regarded as new, is found in the Blue Mountain mining district, Arkansas. When pure, it is a soft, white mineral occurring in large leaves. Analysis gave the following results :—

SiO_2.	Al_2O_3.	Loss on ignition.	Total.
54·32	37·69	7·99	100·00

In this analysis, small proportions of ferric oxide, lime, magnesia, and alkalis have been disregarded. The formula of the mineral is $Al_2O_3,2SiO_2,H_2O$ + Aq.

From the authors' researches it is probable that three members of the kaolin series out of the possible four are known; and the present status of the series may be concisely stated as follows :—

1. Rectorite	$Al_2O_3,2SiO_2,H_2O$ + Aq	Monoclinic (?).
2. Kaolin and members	$Al_2O_3,2SiO_2,2H_2O$	Monoclinic or O.
of the kaolin group	$Al_2O_3,2SiO_2,2H_2O$ + Aq	O.
3. —	$Al_2O_3,2SiO_2,3H_2O$	—
4. Newtonite	$Al_2O_3,2SiO_2,4H_2O$ + Aq	Rhombohedral.

B. H. B.

New Analyses of Astrophyllite and Tscheffkinite. By L. G. Eakins (*Amer. J. Sci.*, **42**, 34—37).—1. *Astrophyllite.*—From a discussion of the analyses published by Bäckström and by König, Brögger deduces the general formula $R''_4R'_4Ti(SiO_4)_4$ for this mineral. The new analysis made by the author closely confirms this formula, agreeing with it better than those from which it was derived. Calculating the small amount of ferric oxide present in with the R'' group, the molecular ratios of the author's analysis give the following elementary proportions :—

$$Si_{587}O_{2389}Ti(Zr)_{153}R''_{536}R'_{234}H_{464}.$$

which reduces to

$$Si_4O_{16\cdot3}Ti_{1\cdot04}R''_{3\cdot65}(R'H)_{4\cdot7}.$$

2. *Tscheffkinite.*—A fragment of this rare mineral from Bedford Co., Virginia, analysed by the author, showed a distinctly banded structure of lustrous black and dull-black material. The analyses, however, show that these two bands are practically identical, the dull being somewhat more hydrated. The molecular ratios seem to lead to no definite or satisfactory formula, a result quite in accordance with the evidence furnished by the microscopic examination of sections.

B. H. B.

Minerals in Hollow Spherulites of Rhyolite. By J. P. Iddings and S. L. Penfield (*Amer. J. Sci.*, **42**, 39—46).—The occurrence of fayalite with other minerals in the lithophysæ and hollow spherulites at Obsidian Cliff has been described by the authors (Abstr., 1891, 26), and they have also called attention to the occurrence of fayalite in obsidian at Lipari and Vulcano (Abstr., 1891, 158). In the present paper, they contribute further to the knowledge of these aqueo-igneous products in siliceous lavas by describing a somewhat different development of hollow spherulites in rhyolites at Glade Creek, Wyoming. In this rhyolite, as in the obsidian of Obsidian Cliff, fayalite occurs in association with abundant quartz, as the result of the mineralising action of vapours in the cooling acid lavas. The quartz in both localities has an unusual, simple, and perfect development, and is accompanied by an uncommon form of sanidine and by tridymite. Moreover, in certain hollow spherulites the fayalite is replaced by hornblende and biotite.

B. H. B.

Siliceous Sand of Monte Soratte. By G. Giorgis (*Gazzetta*, **21**, 514—516).—At St. Oreste, near Monte Soratte, there is a deposit of quartzose sand of the pliocene age lying unconformably on the jurassic limestone of the district. Microscopically it is seen to consist of quartz, orthoclasic felspar, and small quantities of mica. Its composition is as follows:—

Water at 100° = 0·20 *per cent.*

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alkalis.
Dry residue.....	93·50	3·62	traces	traces	—	2·88
Ditto after levigation.....	94·48	2·99	0·11	—	—	2·42

S. B. A. A.

Reproduction of Acid Rocks. By H. Le Chatelier (*Compt. rend.*, **113**, 370—373).—The distinctness, purity, and uniform development of felspar crystals show undoubtedly that they have been formed within a fluid mass and not from a solid mass under the influence of mineralising agents, or from the devitrification of a glass The great pressure under which crystallisation takes place has prevented the felspar from becoming vitreous or amorphous, as it does when heated under atmospheric pressure. Experiments made under a pressure of

5000 atmos. gave only glasses, probably because cooling took place much too rapidly. C. H. B.

Kamacite, Tænite, and Plessite, from the Welland Meteoric Iron. By J. M. Davison (*Amer. J. Sci.*, **42**, 64—66).—The Welland siderolite was described by E. E. Howell (*Proc. Rochester Acad. Sci.*, 1890, 86—87). Its analysis gave 91·17 per cent. of iron, and 8·54 per cent. of nickel. It is singularly free from troilite and schreibersite, and thus offered a good opportunity for the analysis of its separated nickel-iron alloys. Between the decomposed outside and the compact centre there was a zone in which the oxidation was superficial, and confined to the planes of contact of the different alloys that form the Widmanstätten figures. It thus became possible to separate the kamacite and tænite in quantities sufficient for analysis. It was intended to analyse the plessite as a whole; but, on examination, its fine layers were so suggestive of kamacite and of tænite that an attempt was made to analyse them separately. The analytical results were as follows, the analyses of kamacite and tænite being given, each next to its corresponding part of the plessite:—

		Plessite.		
	Kamacite.	Kamacite-like part.	Tænite-like part.	Tænite.
Fe....	93·09	92·81	72·98	74·78
Ni ...	6·69	6·97	25·87	24·32
Co....	0·25	0·19	0·83	0·33
C	0·02	0·19	0·91	0·50
	100·05	100·16	100·59	99·93

The physical and chemical correspondences appear to justify the conclusion that in the Welland meteoric iron there are but two distinct nickel-iron alloys—kamacite and tænite, and that the so-called plessite consists merely of thin, alternating lamellæ of these two alloys. It is unsafe to generalise on a single analysis; but an examination of the markings of other meteoric irons suggests the thought that in them also there may be but two distinct alloys.

B. H. B.

A Gold-bearing Hot-spring Deposit. By W. H. Weed (*Amer. J. Sci*, **42**, 166—169).—The author has examined a series of specimens from the Mount Morgan gold mine, Queensland, with a view to compare them with the siliceous sinters from the hot-spring region of the Yellowstone Park. These specimens possess unusual interest, inasmuch as the observations of the Government Geologist of Queensland show that the Mount Morgan mine, which paid a dividend of £1,200,000 in 1889, works a deposit of a hot spring, the ore being a siliceous sinter impregnated with auriferous hæmatite (compare Abstr., 1886, 21). The Steamboat Springs of Nevada are surrounded by deposits of sinter, in the fissures of which ore deposition is now taking place, a small amount of gold being found in these contemporaneous mineral veins. The Mount Morgan deposit is, however, the only hot-spring deposit known that has been found to contain

gold in workable quantities. A careful search for such deposits has been made for the past eight years in the Yellowstone Park, the most remarkable hot-spring district of the world, without bringing to light a single case of the sort. Hot-spring waters and deposits have been most carefully analysed, without indicating the presence of even a trace of the precious metals. B. H. B.

Note by Abstractor.—In discussing the origin of the Mount Morgan deposit, the author accepts Mr. R. L. Jack's theory, that the deposit is that of a geyser, without pointing out that the origin of this ore-deposit has been the theme of much controversy. According to some, the deposit is thought to be an auriferous zone traversed by a series of quartz veins of auriferous mundic. Others think that it is the decomposed cap of a large pyrites lode. The last contribution to the discussion is afforded by a paper read before the American Institute of Mining Engineers, in June, 1891, by Mr. T. A. Rickard, who advocates the theory of metamorphosis and replacement. The ore-deposit, he thinks, represents an altered portion of shattered country rock, which, by reason of its crushed condition, was readily acted on by mineral solutions, and that these solutions replaced the basic and felspathic with acid and quartzose material, which was also auriferous. It is its quartzose and permeable character which has saved from disintegration the mass thus affected, and has preserved it as an ore-body on the summit of the hill.

Analysis of a Hot Mineral Spring at Sclafani. By E. Paternò (*Gazzetta*, **21**, ii, 40—51).—This water issues at a temperature of 32·9°, and has a sp. gr. of 1·0074 compared with water at 0°. It contains 0·1982 gram per litre of free carbonic anhydride, 0·0171 gram of free hydrogen sulphide, and 16·9 c.c. of nitrogen per litre. The total weight of carbonic anhydride per litre is 0·3527 gram, and of hydrogen sulphide 0·0185 gram. The residue from a litre, when dried at 110°, weighs 12·510 grams.

One litre of the water contains in grams:

SiO_2.	SO_3.	Cl.	Br.	I.	CaO.	SrO.
0·0746	0·0790	6 6900	0·0148	0·0062	0·4720	0·1145

MgO.	Na_2O.	K_2O.	Fe_2O_3 and Al_2O_3.
0·3550	5·5512	0·0170	0·0015

together with 0·0003 gram of organic matter and traces of phosphoric acid, lithium, barium, and manganese. The results obtained differ considerably from those published by Cappa in 1847. W. J. P.

Organic Chemistry.

Constitution of Mercuric Fulminate. By A. F. Hollemann (*Rec. Trav. Chim.*, **10**, 65—84; compare Abstr., 1891, 64).—In order to determine whether mercuric fulminate contained the same empirical

group, $C_2N_2O_2$, as the "dinitrosacyls" (Abstr., 1889, 49), the author studied the action of benzoic chloride on dry mercuric fulminate, and found that a dibenzoylcarbamide was formed. In the course of further experimental work, which is here described at some length, he has determined this to be symmetrical and to be identical in melting point (197°) and physical characters with the dibenzoylcarbamide obtained by the action of guanidine carbonate on anhydrous benzoic acid (Creath, *Ber.*, **7**, 1739), and with that described by Buddéus (Abstr., 1890, 1253). Schmidt's statement that dibenzoylcarbamide yields benzamide when boiled with potassium hydroxide solution (this Journal, 1872, p. 718) is incorrect. The author has previously pointed out the analogy which this formation of a substituted carbamide presents to the conversion of isocyanic acid into an analogous substance, whilst Scholl (Abstr., 1891, 282) obtained acetylisocyanic acid by the action of acetic chloride on mercuric fulminate. From this it would seem that the formation of dibenzoylcarbamide is also due to the formation of an isocyanic derivative. Kekulé's formula, $CN\cdot CH_2\cdot NO_2$, neither explains these results nor the fact that carbamide is formed on the decomposition of copper ammonium fulminate by hydrogen sulphide (Gladstone, *Quart. Journ. Chem. Soc.*, **1**, 228), nor Steiner's observation (this Journal, 1875, p. 882), that urea and guanidine result from the action of ammonia on mercuric fulminate. Steiner's formula, $OH\cdot N{:}C{:}C{:}N\cdot OH$, explains these reactions, but not the formation of chloropicrin and of cyanogen chloride by the action of chlorine water on mercuric fulminate. Regarding fulminic acid as a desmotropic compound, the author suggests the following tautomeric formula, which he thinks Divers' results (Trans., 1884, 13) support:

$$\text{I.}\quad \begin{matrix} C{:}NOH \\ \| \\ C{:}NOH \end{matrix} \rightarrow \begin{matrix} HC{:}NO \\ | \\ HC{:}NO \end{matrix} \rightarrow \begin{matrix} H_2\cdot C\cdot N{<}^{O} \\ | \\ CN \end{matrix}{}_{O} \quad \text{II.}$$

To demonstrate the presence of the nitro-group in the molecule, an attempt was made to synthesise mercuric fulminate by the action of monobromonitroethane (1 mol.) on a solution of mercuric oxide (1 mol.) and mercuric cyanide (1 mol.), but a red precipitate of the compound $CHgBr_2NO_2$ was alone obtained, which neither detonated on percussion nor on heating, and yielded with potassium cyanide the salt $KBr,HgCy_2 + 2H_2O$. A further attempt to prove the presence of a nitro-group by the action of chlorine-water led to no definite result, a very complicated reaction ensuing.

Mercuric fulminate (1 mol.) absorbs dry chlorine (4 atoms) without evolution of any gaseous product, and is converted into a yellow mass of pungent odour which is soluble in cold water, and is probably dichloronitroacetonitrile. Bromine vapour is absorbed by the fulminate in the same ratio, and steam distillation of the resulting yellow mass affords a liquid of irritating odour, which soon solidifies to yield crystals of dibromacetonitrile melting at 60°; the latter can also be separated from a slight residue of mercuric bromide by exhausting the crude product of the reaction with light petroleum. Scholl and the author consider dinitroacetonitrile to be a nitro-derivative. Provided no oxidation occurred in the action of dry

chlorine on mercuric fulminate, the study of dinitroacetonitrile should determine the validity or otherwise of Kekulé's formula.

T. G. N.

Constitution of Allyl Cyanide. By F. Lippmann (*Monatsh.*, **12**, 402—409).—The so-called allyl cyanide was prepared according to the directions of Rinne and Tollens (*Annalen*, **159**, 105), excepting that allyl bromide was substituted for allyl iodide in the process; 50 per cent. of the theoretical yield of cyanide boiling at 118° was obtained. In order to prepare the dibromo-additive product, a quantity of the cyanide was cooled in ice, and gradually treated with a molecular proportion of bromine. After 1—2 days, the product, which no longer had the odour of bromine, was mixed with fuming hydrochloric acid, and allowed to remain for 2—3 days, until the liquid assumed a reddish-brown colour. It was then decomposed with water, and the crystalline precipitate thus formed recrystallised, first from ether and afterwards from hot chloroform, when silky scales of *αβ-dibromobutyramide*, $CHMeBr{\cdot}CHBr{\cdot}CO{\cdot}NH_2$, were obtained. It melts at 147—148°, is readily soluble in cold ether and in hot alcohol and chloroform, but loses hydrogen bromide when heated with water.

The acid solution from which the amide was separated by water was shaken with ether. The ethereal extract, on evaporation, gave a crystalline residue, part of which was insoluble in water, and consisted of a further quantity of the amide, whilst the remainder was readily soluble. The aqueous solution, on evaporation in a vacuum, gave white, needle-shaped crystals of *αβ-dibromobutyric acid*, $CHMeBr{\cdot}CHBr{\cdot}COOH$. This acid may be recrystallised from ether and water, in both of which it is readily soluble; it melts at 88—89°, and differs considerably in physical properties from normal dibromobutyric acid, $CH_2Me{\cdot}CBr_2{\cdot}COOH$, which is liquid at ordinary temperatures. The amide, melting at 147—148°, is readily converted into αβ-dibromobutyric acid when heated with fuming hydrochloric acid for five hours at 120°.

The formation of αβ-dibromobutyric acid from the so-called allyl cyanide shows that the constitution of the latter must be $CHMe{:}CH{\cdot}CN$. This is in harmony with the view of Kekulé and of Rinne (*Ber.*, **6**, 386), but does not agree with that of Pinner (*Ber.*, **12**, 2053).

G. T. M.

Direct Synthesis of Primary Alcohols. By P. Henry (*Compt. rend.*, **113**, 368—370).—Monochloromethyl ether, $CH_2Cl{\cdot}OMe$, and the corresponding ethyl compound $CH_2Cl{\cdot}OEt$, react energetically with the organo-zinc compounds. Zinc chloride separates, and, on treating the product with water and distilling, the primary alkyl oxide can be isolated.

The following ethers were prepared:—Primary methyl propyl ether boiling at 41° under a pressure of 761 mm.; sp. gr. = 0·7381 at 20°, by the action of zinc ethyl on monochloromethyl ether. Normal primary butyl methyl ether, by the action of zinc propyl on monochloromethyl ether; it is a colourless liquid with an agreeable

odour, insoluble in water, and boiling at 71° under a pressure of 759 mm.; sp. gr. at 20° = 0·7593. Normal ethyl propyl ether, by the action of monochloromethyl ethyl ether; it boils at 63—64°; sp. gr. at 20° = 0·7474. Ethyl butyl ether, by the action of zinc propyl on monochloromethyl ethyl ether; it boils at 92° under a pressure of 753 mm.

Zinc propyl is produced as easily as zinc ethyl by means of Gladstone and Tribe's zinc-copper couple, but the yield is only 70 to 75 per cent., propylene and propane being liberated.

C. H. B.

Oxidation of Tertiary Alcohols. By G. Wagner (*J. pr. Chem.* [2], **44**, 308—312).—The oxidation of the tertiary alcohols has heretofore always been effected by chromic acid mixture, which, however, is acknowledged to convert them, by dehydration, into corresponding olefines, so that the products of the oxidation have been those derived from the olefines, rather than true oxidation products of the tertiary alcohols (compare Abstr., 1883, 566; 1886, 437). For this reason the author has experimented with a neutral solution of potassium permanganate as an oxidising agent for tertiary alcohols. He finds that trimethylcarbinol is scarcely attacked by an alkaline 4 per cent. solution of potasssium permanganate even when warmed; and that tertiary amyl alcohol is oxidised by the same solution at the ordinary temperature, but even after a month, the reaction is not complete.

Dimethylisopropylcarbinol (b. p. 117—118°), however, is readily oxidised to pinacone by a neutral aqueous solution of potassium permanganate, and the process adopted is fully described in the paper. This is the first case in which a saturated monhydric alcohol has been directly converted into the corresponding dihydric alcohol.

From this result, the author concludes that the oxidation of tertiary alcohols results in the hydroxylising of one of the carbon atoms which are directly linked to the C(OH) group, a reaction similar to that observed in the oxidation of the ketones, and probably conforming to the same rules (compare this vol., p. 35). A. G. B.

Xylose. By G. Bertrand (*Bull. Soc. Chim.* [3], **5**, 554—557).—Xylose may be obtained from wheat or oat straw by the following process, which is stated to be less laborious than that used by Wheeler and Tollens (Abstr., 1889, 847) in preparing it from pine wood. The straw is extracted with tepid water, and is then boiled for several hours with dilute (1—2 per cent.) sulphuric acid. The liquor, after removal of the sulphuric acid by barium hydroxide, is concentrated on the water-bath, and treated with alcohol, thus yielding an extract from which xylose is obtained as a yellow syrup on removing the solvent. The syrup crystallises on the addition of a crystal of xylose, and the product is recrystallised from hot alcohol. The yield from wheat straw is 2 per cent., from oat straw 4 per cent.

When xylose is treated with sodium amalgam, *xylitol* is obtained as a syrup, which, like sorbitol and perseïtol, and unlike arabitol, gives, with benzaldehyde in the presence of sulphuric acid an abundant precipitate, which appears to have the composition $C_5H_8O_5(CHPh)_2$. The xylitol may be recovered from the compound

by hydrolysis, and, as thus obtained, is a rather sweet, faintly dextrorotatory syrup. *Pentacetylxylitol* is obtained as a syrup, when anhydrous xylitol is treated with acetic anhydride in the presence of zinc chloride.

Xylose is further distinguished from arabinose by the fact that the cadmium salt of its first oxidation product, xylonic acid, forms well-defined, crystalline, double salts with cadmium bromide and chloride; the reaction is very sensitive, as it is visible when only a few milligrams of the sugar is present. The xylose (1 part) dissolved in water (5 parts) is treated with bromine (1 part), and, after 24 hours, the excess of bromine is evaporated off. If the bromine compound is required, the residue is now saturated with cadmium carbonate, concentrated, and precipitated with alcohol; whilst, if the chlorine compound is wanted, the hydrogen bromide is removed by means of lead carbonate, cadmium carbonate and chloride are added to the impure *xylonic acid* thus obtained, and the operation is completed as before.

Jn. W.

Constitution of Xylitol and Xylose. By G. Bertrand (*Bull. Soc. Chim.* [3], **5**, 740—742; compare preceding abstract).—When xylitol is treated with a mixture of nitric and sulphuric acids, it yields a *pentanitrate*, $C_5H_7(NO_3)_5$, as a colourless, insoluble syrup, which is heavier than water, can be exploded by percussion, and burns rapidly without leaving any residue.

By heating xylitol with amorphous phosphorus and iodine in a stream of carbonic anhydride, it is converted into a secondary amyl iodide, which boils at 146°, and yields, on prolonged heating with lead hydroxide and water, methylpropylcarbinol, boiling at 119°.

Xylitol is thus an open-chain pentahydric alcohol, of which xylose is the aldehyde; the two substances being represented by the formulæ $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH$ and $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CHO$.

Jn. W.

Epichloramine. By R. Schiff (*Gazzetta*, **21**, ii, 1—6).—Equivalent weights of epichlorhydrin and ethyl acetoacetate are mixed with excess of alcoholic ammonia solution and left for some hours; there is a slight development of heat, and the reaction is completed by heating on the water-bath for 15 minutes; on the addition of water, a colourless oil is obtained, which soon solidifies to acicular crystals. When recrystallised from dilute alcohol, the new compound has the composition $C_9H_{16}NO_3Cl$, melts at 95° without decomposition, and is not altered by heating for some time at 100—110°. It dissolves in acids to form salts, and is precipitated unchanged from the solution by alkalis; it is moderately soluble in absolute alcohol, less so in ether, and very sparingly in cold water; it separates from its hot aqueous solution in long needles. The solution is not precipitated by silver salts or by picric acid and sodium carbonate, and does not yield a platinochloride. No acetyl derivative could be prepared.

If, in the preparation of this substance, the heating on the water-bath be too prolonged, a whitish, slightly crystalline substance is deposited, which is insoluble in all ordinary solvents, and has the

composition $C_{12}H_{27}N_3Cl_4O_4$; it appears to be identical with the chlorhydrinimide of Claus (Abstr., 1873, 1121).

When the substance $C_9H_{16}NO_3Cl$, is dissolved in hot alcohol, and treated with oxalic acid in alcoholic solution, *epichloramine oxalate*, $(C_3H_8NOCl)_2,H_2C_2O_4$, is obtained as a voluminous, white precipitate, and is purified by solution in water and precipitation by absolute alcohol. It melts at 183—184° with evolution of carbonic anhydride, is moderately soluble in warm water, and almost insoluble in alcohol. In a similar manner, *epichloramine hydrochloride*, C_3H_8NOCl,HCl, is obtained by treating the condensation product with hot dilute hydrochloric acid; on evaporating the solution in a vacuum, the salt is obtained colourless and well crystallised; it is very soluble in water.

Free epichloramine is very soluble in water, and is decomposed by steam distillation with evolution of ammonia: it seems to be very readily converted into condensation products. The author regards it as formed by the condensation of a molecule each of ammonia, epichlorhydrin, and ethyl acetoacetate with elimination of water, and considers that it has probably the constitution

$$CH_2Cl\cdot CH(OH)\cdot CH_2\cdot N{:}CMe\cdot CH_2\cdot COOEt.$$

W. J. P.

Unsaturated Fatty Amines. By C. Paal and A. Heupel (*Ber.*, **24**, 3035—3048; compare Abstr., 1889, 116, and 1890, 399).—*Dibromopropylcarbamide*, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CHBr\cdot CH_2Br$, is prepared by mixing a concentrated aqueous solution of the hydrochloride of dibromopropylamine (compare Henry, *Ber.*, **8**, 399) with potassium cyanate. It melts at 163°, and dissolves easily in alcohol and hot water, sparingly in ether and cold water. An attempt to prepare the analogous thiocarbamide from the hydrobromide of the base and potassium thiocyanate was unsuccessful.

By acting on an alcoholic solution of free propargylamine with ethyl iodide, and allowing the mixture to evaporate in the absence of light, a crystalline residue is obtained, which is separated by treatment with alcohol into *propargylamine hydriodide*, $C_3H_3\cdot NH_2,HI$, which forms lustrous, large, white plates, melting at 205° and sparingly soluble in alcohol, and *diethylpropargylamine hydriodide*, $C_3H_3\cdot NEt_2,HI$, which is easily soluble in alcohol. The silver compound of propargylamine previously prepared was found to have a variable constitution, but undoubtedly contains oxygen. Propargylamine itself, when boiled with sodium nitrite and a little hydrochloric acid, yields propargyl alcohol; this can be distilled with steam, and if the distillate is collected in an ammoniacal silver solution, a white, explosive silver compound, $C_3H_2Ag\cdot OH$, is formed.

Propargyldithiocarbamic acid, $C_3H_3\cdot NH\cdot CSSH$, is obtained by boiling an alcoholic solution of free propargylamine with excess of carbon bisulphide in a reflux apparatus. It melts at 115°, has a feeble, unpleasant odour, and, when heated, smells like a thiocarbimide. It dissolves easily in aqueous alkalis, mineral acids, hot water, ether, alcohol, and benzene, sparingly in light petroleum and cold water. From dilute alcohol, it crystallises in white needles; from a mixture

of benzene and light petroleum in long plates. Acetic acid and dilute mineral acids precipitate it from solutions of its alkali salts. The barium salt forms a white, flocculent, the stannic a white, gelatinous, the copper a green, flocculent, the lead a white, granular, and the silver salt a white, flocculent precipitate. The silver salt yields silver sulphide when boiled with water. The acid itself is completely oxidised by silver or mercuric oxide.

Propargylphenylcarbamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_3H_3$, is prepared by mixing an aqueous solution of propargylamine oxalate with rather less than the theoretical amount of phenyl cyanate, and adding to the cooled mixture a slight excess of a concentrated solution of potassium carbonate. After shaking for a time, a crystalline product is obtained containing a small quantity of symmetrical diphenylcarbamide, which is easily soluble in hot water, mixed with very sparingly soluble propargylphenylcarbamide; the latter crystallises from water in radiating groups of needles, melts at 133°, and dissolves easily in ether, alcohol, and benzene, sparingly in light petroleum and cold water.

Isobutylallylamine, $C_3H_5{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2$, is prepared by digesting equivalent quantities of allylamine and isobutyl bromide for two or three days at first a gentle heat, finally on the water-bath. The product is diluted with water, acidified, separated from unattacked isobutyl bromide, and treated with caustic soda, and the bases thus liberated are dried with solid potash and fractionally distilled. Some *diisobutylallylamine*, $C_3H_5{\cdot}N(C_4H_9)_2$, boiling at about 165°, was isolated, but the main product is isobutylallylamine, a colourless, volatile liquid boiling at 123° (uncorr.), and having a penetrating odour resembling that of allylamine. It is soluble in water. The *hydrochloride*, $C_7H_{15}N,HCl$, crystallises in white, lustrous, hygroscopic plates which melt at 216°, and are fatty to the touch. The *aurochloride*, $C_7H_{15}N,HAuCl_4$, crystallises from hot water in splendid, yellow needles which melt at 140°, and slowly decompose when boiled with water. The *platinochloride*, $(C_7H_{15}N)_2,H_2PtCl_4$, crystallises from alcohol in splendid, red needles, melts at 182°, and dissolves easily in alcohol and water. The *hydrobromide*, $C_7H_{15}N,HBr$, crystallises from a mixture of alcohol and ether in white plates which have a silky lustre; it melts at 222° and dissolves readily in water and alcohol. The *acid oxalate*, $C_7H_{15}N,C_2H_2O_4$, crystallises from alcohol in small, white plates, melts at 221°, and dissolves fairly easily in water, sparingly in alcohol.

Isobutylallylphenylcarbamide, $C_4H_9{\cdot}N(C_3H_5){\cdot}CO{\cdot}NHPh$, is formed by the union of isobutylallylamine with phenyl cyanate at the ordinary temperature. A viscid, colourless oil is obtained, which very slowly becomes crystalline. It is insoluble in water, but soluble in alcohol, benzene, and light petroleum, and crystallises from the last solvent in aggregates with a radial structure which melt at 37—39°.

Isobutylallylphenylthiocarbamide, $C_4H_9{\cdot}N(C_3H_5){\cdot}CS{\cdot}NHPh$, is obtained by mixing equivalent quantities of isobutylallylamine and phenylthiocarbimide. It forms a viscid colourless oil which slowly crystallises in long, colourless needles grouped like ice-flowers. It melts at 41—43°, and dissolves readily in ether, ethyl acetate, alcohol, and benzene, sparingly in light petroleum and not at all in water.

Isobutylpropargylamine, $C_4H_9{\cdot}NH{\cdot}C_3H_3$, was prepared by gradually adding isobutyldibromopropylamine hydrobromide, $C_4H_9{\cdot}NH{\cdot}C_3H_5Br_2$, to a well-cooled alcoholic solution of sodium ethoxide, and finally heating the mixture in well-corked bottles in the water-bath. The contents were then diluted with water and distilled with steam until an oily base that was also formed began to come over. The distillate was concentrated, treated with a large excess of potassium carbonate, and the bases extracted with ether. The ethereal solution was dried with solid potash and fractionally distilled; by this means, isobutylpropargylamine was isolated as a colourless, volatile liquid, boiling at 134—136° (uncorr.), miscible in all proportions with water and having an odour which recalls that of ammonia, and at the same time that of camphor. Its aqueous solution precipitates iron hydroxide from a solution of the chloride, has no effect on an ammoniacal copper solution, and with an ammoniacal silver solution yields a silver compound as a white precipitate which is fairly stable while moist, but explodes easily when dry. The *oxalate*, $C_7H_{13}N,C_2H_2O_4$, forms lustrous, white needles or plates melting at 210°; it can be crystallised from alcohol or from water. It reduces a solution of gold chloride only very slowly (*allylamine oxalate* itself, $C_3H_5{\cdot}NH_2,C_2H_2O_4$, which forms radiating groups of white needles melting at 120°, effects this reduction even more slowly). The *hydrochloride*, $C_7H_{13}N,HCl$, crystallises from a mixture of alcohol and ether in large, lustrous, white plates melting at 148° and dissolving readily in water and alcohol. The *platinochloride*, $(C_7H_{13}N)_2,H_2PtCl_6$, separates from alcohol in ill-defined, red, crystalline aggregates which melt at 172°, and are decomposed when kept for a short time at 100°.

Isobutylpropylamine, $C_4H_9{\cdot}NHPr^a$, is obtained by reducing isobutylpropargylamine in alcoholic solution with metallic sodium, the mixture being heated on the water-bath. The product formed was diluted with water and distilled with steam; the distillate acidified with hydrochloric acid, evaporated to a small bulk, and treated with potash; the oily layer was removed, dried with solid potash, and fractionally distilled, finally over metallic sodium. The base is a colourless, volatile liquid boiling at 123—125°, miscible with water in all proportions, and very similar to isobutylallylamine. The *hydrochloride*, $C_7H_{17}N,HCl$, dissolves easily in water and alcohol, and crystallises from a mixture of alcohol and ether in small plates which melt at 135°. The oxalate, $C_7H_{17}N,C_2H_2O_4$, crystallises from alcohol in small, white needles melting at 224°. C. F. B.

Crotonaldoxime. By T. Schindler (*Monatsh.*, **12**, 410—418).—This compound is obtained when 2 mols. of crotonaldehyde (compare Lieben and Zeisel, *Monatsh.*, **1**, 20) is slowly added during continued agitation to a cold solution of 3 mols. of hydroxylamine hydrochloride which has been carefully neutralised with sodium carbonate, and the resulting carbonic anhydride completely removed by shaking. The product is extracted with ether, and the ethereal solution distilled until the greater portion of the ether is removed. The concentrated solution is allowed to evaporate spontaneously, when an oil

having a characteristic odour separates, and in this oil a number of stout, closely striated prisms of *crotonaldoxime*, C_4H_7ON, slowly form. The compound is insoluble in water, but readily dissolves in ether, alcohol, chloroform, and hot benzene, and may be best recrystallised from the last-named solvent, when it forms colourless, odourless, volatile crystals which melt at 119—120°. On heating with acetic anhydride for two hours in a reflux apparatus, the aldoxime is converted into crotononitrile, C_4H_5N, a product which boils at 117·4—118·4°; has a sp. gr. of 0·8468 at 0° compared with water at 4°, and is apparently identical with that obtained by Rinne and Tollens (*Annalen*, **159**, 105) from allyl iodide and potassium cyanide. Tollens (*loc. cit.*) and Pinner (*Ber.*, **12**, 2053) have erroneously attributed the formula $CH_2{:}CH{\cdot}CH_2{\cdot}CN$ to this compound, which, as shown by its production from crotonaldoxime, $CHMe{:}CH{\cdot}CH{:}NOH$, must really be $CHMe{:}CH{\cdot}CN$ (compare Kekulé, *Ber.*, **6**, 386). On the addition of bromine and subsequent digestion with concentrated hydrochloric acid, the nitrile is converted into a mixture of *dibromobutyramide*, $CHMeBr{\cdot}CHBr{\cdot}CONH_2$, which melts at 148—149°, and *αβ-dibromobutyric acid*, $CHMeBr{\cdot}CHBr_2{\cdot}COOH$, which melts at 87—90° (compare Lippman, this vol., p. 27). When the aldoxime is reduced by Goldschmidt's method (Abstr., 1887, 568), crotylamine, $C_4H_7NH_2$, which boils at 81—85°, is obtained.

The oil from which the crotonaldoxime separates is a very inactive substance, and does not readily lend itself to purification. Since, on elementary analysis, it gives numbers which very closely correspond with those required for the formula of crotonaldoxime itself, the author suggests that it may possibly be the stereoisomeride of the formula $C_3H_5{\cdot}CH{:}N{\cdot}OH$ (compare Hantzsch, Abstr., 1891, 439).

G. T. M.

The Oximes of Chloral and Butyl Chloral. By R. Schiff and N. Tarugi (*Gazzetta*, **21**, ii, 6—12).—Nägeli (Abstr., 1883, 728) prepared a dichloroglyoxime, $OH{\cdot}N{:}CCl{\cdot}CCl{:}NOH$, in small quantities by the action of free hydroxylamine on chloral hydrate. The authors find that *chloraldoxime* is easily prepared by boiling an aqueous solution of equivalent proportions of chloral hydrate and hydroxylamine hydrochloride (compare V. Meyer, Abstr., 1891, 1181). On cooling, a yellowish or greenish oil separates, having an odour closely resembling that of free chlorine. It could not be obtained in a state sufficiently pure for analysis; if left to itself, or treated with hot water, it decomposes with evolution of hydrogen chloride and hydrogen cyanide, probably in accordance with the following equation:—$CCl_3{\cdot}CH{:}NOH = HCN + COCl_2 + HCl$.

Butylchloraldoxime, $CHMeCl{\cdot}CCl_2{\cdot}CH{:}NOH$, is readily prepared by pouring boiling water on a dry mixture of equivalent proportions of butyl chloral hydrate and hydroxylamine hydrochloride; the oxime separates as an oil which solidifies on cooling. A still better method of preparation is to pour the cold solution of the hydroxylamine hydrochloride on the dry butyl chloral hydrate, and allow it to remain for some days; the theoretical yield of pure oxime is thus obtained. Butyl chloraldoxime is fairly soluble in all the usual solvents excepting water; it crystallises from light petroleum in very

large, opaque octahedra, and melts at 65° without decomposition. It dissolves in cold, concentrated sulphuric acid, and is precipitated unaltered by water; on heating the solution, however, hydrogen chloride is evolved. It is extremely sensitive towards alkalis, and even when washed with ordinary tap-water, rapidly turns yellow and green. *Acetylbutyl chloraldoxime*, $C_6H_8Cl_3NO_2$, is obtained by gently heating the oxime in acetic anhydride solution; it is a white substance melting at 63—64°. If the heating be too prolonged, decomposition occurs with evolution of hydrogen chloride and hydrogen cyanide.

On heating with alkalis or alkali carbonates, butyl chloraldoxime becomes first green and finally bright yellow, hypochlorous acid being formed. If the reaction is arrested at the green stage, a yellow powder is obtained having the composition $C_8H_{12}Cl_3N_2O_3$.

When a few drops of glacial acetic acid are added to an alcoholic solution of the oxime (1 mol.) containing litharge (2 mols.), lead chloride is formed, and a colourless, well crystallised substance is obtained which melts with decomposition at 158°. This is probably *dichlorocrotonaldoxime*, CMeCl:CCl·CH:NOH.

The study of butyl chloraldoxime is being continued.

W. J. P.

Sulphinic Derivatives and their Analogies to Compounds of Organic Amines. By R. Nasini and T. Costa (*Gazzetta*, **21**, 554—565).—It was previously shown by the authors (Abstr., 1891, 1305) that the molecular refractive energy of sulphur in the derivatives of triethylsulphine is extremely high, and especial attention was drawn to the iodide, the molecular refractive energy of which remains constant when the concentration is varied, but varies when the solvent is changed. Similarly, aqueous solutions of trimethylsulphine bromide and iodide give very high results for the molecular refractive energy of sulphur. The authors consider that the theory of electric dissociation affords a simple explanation of these facts. Determinations of the molecular weights of the above-mentioned compounds by the cryoscopic method yield approximately normal numbers in aqueous solutions, but the acetic solutions of the chloride and bromide of triethylsulphine yield abnormal results. It is, however, noticeable that the hydrate, chloride, and iodide, which yield successively increasing values for the molecular refractive energy of sulphur, also appear to be successively less dissociated in their solutions. Similarly the iodide of trimethylsulphine appears to be less dissociated than that of triethylsulphine, and the sulphur in the former compound accordingly appears to have a smaller molecular refractive energy. The alcoholic solution of triethylsulphine iodide, in which electrical dissociation cannot take place, in like manner yields the highest value for the molecular refractive energy of sulphur. In acetic acid solutions, the molecule of triethylsulphine iodide appears to be more complex. The molecular weight of triethylsulphine bromide calculated from the rise of the boiling point of an alcoholic solution gave approximately normal results.

The molecular depression of tetrethylammonium iodide in aqueous solution is almost equal to that of the corresponding sulphinic de-

rivative. The refractive energy of tetrethylammonium iodide is greater than the sum of the refractive energies of triethylamine and ethyl iodide, exactly as the refractive energy of triethylsulphine iodide exceeds that of its constituents. The determination of the molecular weight of tetrethylammonium iodide from the rise of the boiling point of an alcoholic solution also yields a normal result.

S. B. A. A.

Oxidation of Mixed Ketones of the Fatty Series. By G. Wagner (*J. pr. Chem.* [2], **44**, 257—308).—Of Popoff's seven rules concerning the oxidation of ketones (*Annalen*, **161**, 299—301: *J. Russ. Chem. Soc.*, **4**, 67), the fourth, or that which is commonly known as "Popoff's rule," asserts that when a ketone whose alcohol radicles are of the same series, but not isomeric, is oxidised, the carbonyl remains linked to the alcohol radicle which is lowest in the series; the fifth states that in a ketone whose alcohol radicles are of the same series and are isomeric, that alcohol radicle in which the least hydrogenised carbon atom is attached to the carbonyl will be the first oxidised.

In this paper, the author details several experiments which are not in accordance with the above rules, and discusses them by the light of the work which has been done on the subject by various chemists.

The experiments, some of which have already been published in *J. Russ. Chem. Soc.*, **16**, 645 and 695 (compare Abstr., 1885, 1197), but have not been copied into other journals, may be summarised here.

Ethyl propyl ketone (b. p. 122—123° at 745 mm.), from the action of zinc ethyl on butyric chloride (b. p. 98—102°), yields butyric, propionic, and acetic acids when oxidised by potassium dichromate and sulphuric acid. The formation of butyric and acetic acids appears to be the primary reaction, the propionic acid resulting from a secondary one; two distinct reactions take place in this way in the oxidation of most mixed ketones, and the proportion of the primary to the secondary reaction approaches 2 : 1, as in this case. Popoff (*Annalen*, **161**, 289) and Völker (*Wien. Acad.* [2], **73**, 335) found that propionic acid was the only product of the oxidation of ethyl propyl ketone; the author can only conclude that they worked with too small quantities of the ketone, and failed to separate the acids.

Ethyl hexyl ketone, obtained by the oxidation of the corresponding secondary alcohol, itself obtained from the action of zinc ethyl on œnanthaldehyde, is a clear, refractive liquid with a sharp, aromatic odour; it crystallises at −8° in long prisms, and boils at 190° (752 mm.); its sp. gr. at 0° = 0·840, at 20°/0° = 0·825. The products of the oxidation of this ketone are œnanthylic and acetic acids from the primary reaction, and caproic and propionic acids from the secondary, the proportion between the two reactions being nearly 3 : 1.

Propyl hexyl ketone, obtained by the oxidation of the corresponding alcohol (b. p. 210—211° at 759 mm.), boils at 206—207° (753 mm.), and solidifies in a freezing mixture to clusters of needles which melt at −9·5° to −9°. Its odour is similar to that of ethyl hexyl ketone;

its sp. gr. at 0° = 0·839, at 20·5°/0° = 0·824. Only œnanthylic and propionic acids could be separated from the product of the oxidation of this ketone.

The above experiments disprove Popoff's fourth rule; the following concern the fifth rule:—

Ethyl isobutyl ketone is formed by the action of zinc ethyl on isopropylacetic chloride (b. p. 116—116·5°). It is a refractive liquid with an odour like peppermint; it boils at 134·5—135° (735 mm.); its sp. gr. at 0° = 0·829, at 17°/0° = 0·815. Isopropylacetic acid boils at 175° (749 mm.). When oxidised, the ketone yields, from the primary reaction, isopropylacetic acid and acetic acid; and from the secondary reaction, isobutyric acid and propionic acid, the primary reaction exceeding the secondary; acetone and dimethacrylic acid (?) are also obtained, probably as secondary oxidation products of the acids. This behaviour shows that the fifth rule is fallacious.

Propyl isobutyl ketone (b. p. 154—156° at 755 mm.) yields isopropylacetic acid, propionic acid, acetone, and acetic acid, when oxidised.

Ethyl isopropyl ketone is prepared from isobutyric chloride (b. p. 92—93°) and zinc ethyl; it boils at 113·75—114° (745 mm.), not 117—119° (Pawloff, *J. Russ. Chem. Soc.*, **8**, 242); its sp. gr. at 0° = 0·830, at 18°/0° = 0·814. It yields on oxidation acetone, propionic acid, isobutyric acid, and acetic acid (compare Pawloff, *loc. cit.*).

Methyl isobutyl ketone boils at 115·5° (745 mm.; Frankland, *Annalen*, **145**, 83, gives 114° at 758°), and has a sp. gr. at 0° = 0·8195 (Frankland gives 0·81892), at 19°/0° = 0·8034. When oxidised, it yields isobutyric and acetic acids from the primary reaction, and isopropylacetic acid and formic acid from the secondary.

Methyl isoamyl ketone (b. p. 144—144·5° at 752 mm.) yields isopropylacetic acid and isobutylacetic acid on oxidation; Popoff obtained valeric and acetic acids.

Methyl butyl ketone yields butyric acid and normal valeric acid on oxidation.

The author deduces the following generalisations from the results of his and of other experimenters' work on this subject:—

1. When a ketone of the fatty series is oxidised, the hydrogen atom attached to one of the carbon atoms linked to the carbonyl is hydroxylised; the molecule of hydroxyl compound thus formed is split up by further oxidation, 2 mols. of fatty acids, or 1 mol. of a fatty acid and 1 mol. of a ketone, being formed.

2. If only one of the carbon atoms linked to the carbonyl be hydrogenised, only this will be oxidised and detached. If, however, both be hydrogenised, chromic acid mixture at 100° will generally cause oxidation in two directions, so that in some molecules of the ketone the one, and in others the other, of these carbon atoms will be oxidised, and there will result a primary and a secondary reaction regulated by the following conditions.

3. If the carbon atoms linked to the carbonyl be unequally hydrogenised, the one which has less hydrogen will be oxidised and eliminated in the primary reaction, and the one which is more hydrogenised, in the secondary reaction.

4. If the carbon atoms be equally hydrogenised but combined, the one with a secondary (or tertiary?), the other with a primary, alcohol radicle, the latter will be oxidised and eliminated.

5. If the carbon atoms linked to the carbonyl be equally hydrogenised and combined with radicles of the same series, but of different molecular weight, that which is combined with the radicle having less carbon will be preferably oxidised and eliminated.

These generalisations allude to the oxidation of ketones at 100° with chromic acid mixture. Experiments made with methyl butyl ketone showed that (1) the course of the oxidation of methyl butyl ketone is influenced by the temperature; (2) at low temperatures, the oxidation proceeds in one direction only, and the less hydrogenised carbon atom attached to the carbonyl is oxidised and eliminated; (3) at higher temperatures, the oxidation extends to both these carbon atoms; (4) it is thus probable that at very high temperatures, if the ketone could withstand such, the course of the oxidation would be in one direction only, and that would be the reverse of (2).

A. G. B.

Determination of the Affinity of Organic Acids by means of Lacmoïd. By F. Röhmann and W. Spitzer (*Ber.*, **24**, 3010—3015). —During the titration of organic acids with soda, the authors have observed that a drop of the liquid brought into contact with red lacmoïd paper produces a blue colour before sufficient soda has been added to form the normal salt; the solution will turn blue lacmoïd paper red, but this red colour disappears before the acid is entirely neutralised. This reaction depends on the fact that the alkali is divided between the lacmoïd and the organic acid in a definite proportion, which varies according to the nature of the acid; a method is thus afforded of determining the relative affinities of acids for alkali. Experiments have shown that the coefficient of neutrality s/s' of two acids is in inverse proportion to their affinity for alkali: s = the quantity of acid which is necessary to bring about the change in colour of the lacmoïd paper, and s' represents the amount of normal salt present. For the full details of calculation the original paper should be consulted.

The affinities of the following monobasic acids, compared with formic acid, agree closely with the values given in Ostwald's tables:— Acetic, propionic, butyric, isobutyric, valeric, hydroxypropionic, and hydroxyisobutyric. The method is also applicable to the bibasic acids, a similar agreement in the results, as compared with other methods, being obtained.

It is desirable to always determine the quantity of alkali which is required to be added to the acid in order to produce a blue colour on red lacmoïd paper, since the inverse procedure is more liable to experimental error.

J. B. T.

Behaviour on Dry Distillation of the Silver Salts of Organic Acids. By J. Kachler (*Monatsh.*, **12**, 338—349).—Silver acetate, on dry distillation, is decomposed according to the equation $4AgC_2H_3O_2 = 4Ag + 3C_2H_4O_2 + C + CO_2$, the reaction being complete at a temperature of 220—240°. The compound furnishes the same products,

and in practically the same proportions, when it is heated to a high temperature with water in sealed tubes.

Silver formate decomposes in accordance with the equation $2AgCHO_2 = CH_2O_2 + CO_2 + 2Ag$, when heated with water in sealed tubes.

The silver salts of isovaleric, normal caproic, and œnanthylic acids, on dry distillation, are approximately decomposed according to the equation $2n(AgC_nH_{2n-1}O_2) = (2n - 1)(C_nH_{2n}O_2) + (n - 1)C + CO_2 + 2nAg$; in fact, this equation appears to indicate the manner in which the silver salts of fatty acids are generally resolved under such conditions.

Silver palmitate, on distillation under reduced pressure (430 mm.), gives a considerable quantity of palmitic acid, and, similarly, the silver salts of lactic, α-hydroxyisobutyric, phenylacetic, and benzoic acids decompose with formation of the respective free acids.

The author confirms the statement of Klimenko (*J. Russ. Chem. Soc.*, **12**, 97), that silver lactate, when air-dried, crystallises with $\frac{1}{2}$ mol. H_2O (compare Engelhardt and Maddrell, *Annalen*, **63**, 90).

G. T. M.

Action of Hydriodic Acid on Amido-acids. By A. Kwisda (*Monatsh.*, **12**, 419—430).—The author finds that the readiness with which hydrogen is substituted for amidogen, on treating the amido-acids with hydriodic acid, varies considerably with the constitution of the acid (see original). In his investigations, the acids under examination, namely, glycocine, α- and β-alanine, leucine, aspartic acid, glutamic acid, and ortho-, meta-, and para-amidobenzoic acids, were heated in sealed tubes with excess of hydriodic acid of sp. gr. 1·96. Monobasic, fatty acids, of the formula $NH_2{\cdot}C_nH_{2n}{\cdot}COOH$, are thereby decomposed, according to the equation $NH_2{\cdot}C_nH_{2n}{\cdot}COOH + 3HI = C_nH_{2n+1}COOH + NH_4I + I_2$, whilst such bibasic acids as aspartic and glutamic acids are converted into monobasic acids, thus:—$NH_2{\cdot}C_nH_{2n-1}(COOH)_2 + 3HI = C_nH_{2n+1}{\cdot}COOH + CO_2 + NH_4I + I_2$; ortho-, meta-, and para-amidobenzoic acids are not decomposed in the same way as the monobasic acids of the fatty series, for, in addition to the chief product, benzoic acid, small quantities of carbonic anhydride and of free hydrocarbons are obtained. The author has not been able to confirm the observation of Rosenstiehl (*Zeit. für Chem.*, 1869, 471) that toluidines are formed on heating amidobenzoic acids with hydriodic acid. G. T. M.

β-Trimethylethylidenelactic Acid. By C. Glücksmann (*Monatsh.*, **12**, 356—361; compare Abstr., 1890, 237).—A more convenient method of preparing trimethyllactic acid than that previously described is as follows:—20 grams of pinacone is suspended in 100 c.c. of 20 per cent. sodium hydroxide solution, and 63 grams of potassium permanganate in a 4—5 per cent. aqueous solution is slowly added to the well-cooled mixture. When the oxidation is complete, the product is filtered, neutralised with sulphuric acid, and evaporated to dryness on the water-bath. The residue is dissolved in the least possible quantity of water, and treated with 250 grams of 4 per cent. sodium amalgam, added a little at a time. The solution is filtered,

acidified with sulphuric acid, extracted with ether, the ethereal solution evaporated, and the residue steam distilled, until the distillate ceases to be acid. The residue, dried in a vacuum over sulphuric acid, consists of trimethyllactic acid.

On heating the acid (1 part) with 90 per cent. sulphuric acid (3—4 parts) in a reflux apparatus at 50°, it is resolved into carbon monoxide, water, and *trimethylacetaldehyde*, $CMe_3{\cdot}COH$ (yield 80 per cent.). The new aldehyde boils at 92—94°, reduces a solution of silver, restores the colour to magenta, which has previously been treated with sulphurous anhydride; and, on oxidation with chromic acid, appears to be converted into acetic acid. G. T. M.

Halogen Derivatives of Malonic Acid. By M. Conrad and C. Brückner (*Ber.*, **24**, 2993—3005). — *Ethyl dichloromalonate*, $CCl_2(COOEt)_2$, is prepared by treating ethyl chloromalonate with chlorine at 120°, removing the excess of the latter and the hydrogen chloride, first by heating on the water-bath, and subsequently by allowing the product to remain over soda-lime in a vacuum, and distilling, when the compound passes over at 231—234° with only slight decomposition as a colourless liquid, having a sp. gr. 1·268 at 17° compared with water at 15°. Treated with an excess of cold alcoholic potash, a mixture of potassium dichloromalonate and mesoxalate appears to be formed; whilst on mixing it with 6—10 times its volume of concentrated alcoholic ammonia, dichloromalonamide, melting at 202° (see Zincke and Kegel, Abstr., 1890, 490), separates after two days, and dichloracetamide (m. p. 98°) is obtained from the filtrate.

Ethyl chlorobromomalonate, $CClBr(COOEt)_2$, is obtained by brominating ethyl chloromalonate; it distils at 136—139° under a pressure of 35 mm., and boils at the ordinary pressure at 239—241° with partial decomposition; its sp. gr. is 1·467 at 16° compared with water at 15°. Treated with four times its volume of concentrated alcoholic ammonia, a compound melting at 160—165° separates, which is, perhaps, a mixture of chlorobromomalonamide and amidochloromalonamide; whilst *chlorobromacetamide* melting at 117° is obtained from the filtrate. Chlorobromacetamide has already been prepared by Cech and Steiner (this Journal, 1876, **1**, 373), and as it differs in melting point from the authors' compound, they have repeated Cech and Steiner's experiments, and find that neither chlorobromacetic acid nor the amide described by these chemists are homogeneous substances, but are contaminated with the dibromo-derivatives. Ethyl bromomalonate, $CHBr(COOEt)_2$ (Knoevenagel, Abstr., 1888, 707), has a sp. gr. of 1·426 at 15° compared with water at the same temperature.

Ethyl acetyltartronate, $OAc{\cdot}CH(COOEt)_2$, is produced together with the *compound* $C(COOEt)_2{:}C(COOEt)_2$, by heating ethyl bromomalonate (88 grams) and potassium acetate (40 grams) dissolved in absolute alcohol, at 40—50°; the former is a bright yellow oil, boiling at 158—163° (60 mm.), and has a sp. gr. 1·131 at 1·95° compared with water at 15°, whilst the latter is a solid compound melting at 56°. When ethyl acetyltartronate is dissolved in ether and treated with

sodium (1 eq.), and then heated for 10 seconds on the water-bath with ethyl iodide, the *ethyl derivative*, $OAc{\cdot}CEt(COOEt)_2$, boiling at 151—153° (30 mm.) is formed.

Ethyl mesoxalate, $C(OH)_2(COOEt)_2$, described by Petrieff as an oil, is obtained by treating ethyl acetyltartronate with somewhat more than one molecular proportion of bromine at 110°: it boils at 140—145° (50 mm.), solidifies after a time, and when crystallised from ether melts at 57°.

Ethyl phenyltartronate, $OPh{\cdot}CH(COOEt)_2$, is prepared by dissolving sodium (2·3 grams) in alcohol (35 c.c.), adding phenol (9·4 grams) and ethyl bromomalonate (24 grams), heating, distilling off the greater portion of the alcohol, adding water, and extracting the precipitated oil with ether; it distils under a pressure of 60 mm. at 230—240°. The acid obtained on hydrolysis with hydrochloric acid yields phenylglycollic acid (m. p. 96°) when heated at 180°.

Ethyl dibromomalonate, $CBr_2(COOEt)_2$ (J. Wislicenus, Abstr., 1888, 151), is obtained by brominating ethyl malonate in direct sunlight; it distils at 145—155° under a pressure of 25 mm.; when dissolved in half its volume of cooled, concentrated, alcoholic ammonia, crystals separate, after a time, of a compound which probably consists of *diamidomalonamide*, $C(NH_2)_2(CONH_2)_2$: this darkens at 150°, dissolves in water with decomposition, and loses ammonia when carefully heated at 90—100°, yielding *imidomalonamide*, $NH{:}C(CONH_2)_2$, a compound dissolving in water to a neutral solution, from which ammonia is evolved on heating. When ethyl dibromomalonate is heated with benzene and sodium in the form of wire, it yields the *compound* $C(COOEt)_2{:}C(COOEt)_2$ (see above); if digested with an alcoholic solution of potassium acetate, ethyl mesoxalate is formed; whilst when heated with a mixture of phenol and sodium ethoxide, *ethyl diphenoxymalonate*, $C(OPh_2)(COOEt)_2$, is obtained distilling at 250—260° under a pressure of 60 mm., and this, on boiling with alcoholic potash, yields the corresponding *acid*, which, after being crystallised from water, melts at 173°.

Bromethylmalonic acid, $CEtBr(COOH)_2$, is obtained in theoretical yield when ethylmalonic acid is heated on the water-bath with an excess of bromine; it melts at 104° with the evolution of carbonic anhydride and the formation of bromobutyric acid. A. R. L.

Action of Zinc on Ethyl Dibromosuccinate. By A. Michael (*J. pr. Chem.* [2], **44**, 399—403).—In this paper the author replies to the criticisms of Claus (Abstr., 1891, 1338) on the work which Michael and Schulthess published on the subject (Abstr., 1891, 1184). The discussion is now closed as far as the author is concerned.

A. G. B.

Decomposition of Glutaric Acid at a High Temperature. By A. Claus (*Annalen*, **265**, 247—253).—In reply to Wisbar (Abstr., 1891, 1011), the author states that a careful repetition of his previous experiments has proved conclusively that carbonic anhydride is evolved on heating glutaric acid under the conditions already described. When the acid is kept for a long time at 180—210°, it is converted into its anhydride; this compound is then completely

decomposed with evolution of carbonic anhydride, and there remains a porous, carbonaceous mass; the liquid distillate contains a considerable quantity of an acid, which is not butyric acid, as was first stated; the investigation of this product will be continued.

F. S. K.

Synthesis of Polybasic Fatty Acids. By K. Auwers, E. Köbner, and F. v. Meyenburg (*Ber.*, **24**, 2887—2901).—In a previous paper (Abstr., 1891, 307), Auwers has published a preliminary account of the synthesis of polybasic acids; the present communication gives a detailed account of the acids already prepared. The process employed is the same in all cases, and consists in warming a mixture of a solution or emulsion of the sodium compound of ethyl malonate or one of its alkyl derivatives with the ethyl salt of an unsaturated acid. The product is mixed with water and dilute sulphuric acid, and the oily, ethereal salt which separates washed, dried, fractionated under reduced pressure, and hydrolysed by boiling with a mixture of equal volumes of concentrated hydrochloric acid and water.

The preparation of symmetrical $\alpha\alpha$-dimethylglutaric acid has already been described (*loc. cit.*). *β-Methylglutaric acid*,

$$COOH{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}COOH,$$

is formed by the action of ethyl crotonate on ethyl sodiomalonate, and hydrolysis of the crude ethyl salt first obtained; after crystallisation from ether and benzene, it melts at 86°. Ethyl sodiomalonate and ethyl fumarate yield as the first product *ethyl propanetetracarboxylate*, $CH(COOEt)_2{\cdot}CH(COOEt){\cdot}CH_2{\cdot}COOEt$, which boils at 200—220° under a pressure of 25 mm., and on hydrolysis yields tricarballylic acid, $COOH{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH$, melting at 162—164°. The authors confirm Emery's statement that this acid, on treatment with acetic acid, yields an *anhydrotricarballylic acid*, $C_6H_6O_5$, melting at 131° (Abstr., 1891, 689).

The product of the reaction of ethyl fumarate and ethyl sodiomethylmalonate is an ethyl salt which boils at 196—198° under a pressure of 20 mm., and has a sp. gr. of 1·1158 at 18°/4°. On hydrolysis, it yields two acids of the composition $C_7H_{10}O_6$, which must, from their mode of formation, both be *α-methyltricarballylic acid*, $COOH{\cdot}CHMeCH(COOH){\cdot}CH_2{\cdot}COOH$, and represent stereometric isomerides, an acid of this formula having two asymmetrical carbon atoms. The acids are separated by crystallisation from water; the less soluble compound crystallises in compact, lustrous prisms, melts at 180°, is readily soluble in alcohol and acetone, but almost insoluble in benzene and light petroleum; its *silver* salt, $C_7H_7Ag_3O_6$, is a heavy, white precipitate. The more soluble acid is contained in the mother liquor of the previous acid, and is separated by repeated crystallisation from water; it still, however, contains ammonium chloride derived from the ethyl cyanacetate present in commercial ethyl malonate, and may be separated from it by treatment with anhydrous ether. It then melts at 134°, and in its other properties closely resembles the isomeric acid, into which it is partially converted by heating with hydrochloric acid at 200°.

The action of ethyl sodiomalonate on ethyl citraconate might proceed in two different ways, giving rise either to an α- or a β-methyltricarballylic acid. The intermediate ethereal salt boils at 226° under a pressure of 39 mm., and on hydrolysis yields in small quantity an acid which has the composition $C_7H_{10}O_6$, forms beautiful, transparent crystals, and melts at 164°. It is not identical with either of the foregoing acids, and must therefore be *β-methyltricarballylic acid*, $COOH{\cdot}CH_2{\cdot}CMe(COOH){\cdot}CH_2{\cdot}COOH$. If ethyl itaconate be substituted for ethyl citraconate, two reactions are also possible, leading to the formation of either β-methyltricarballylic acid or butanetricarboxylic acid. The intermediate ethyl salt was found to boil at 200—240° under 37 mm. pressure, whilst the acid formed from it crystallises in rosette-shaped aggregates of prisms, and melts at 116—120°. It differs, therefore, completely from β-methyltricarballylic acid, and must be *butanetricarboxylic acid*,

$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH.$$

The two stereoisomeric *α-ethyltricarballylic acids*,

$$COOH{\cdot}CHEt{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH,$$

may be prepared in a manner exactly similar to the corresponding methyl compounds. The intermediate ethyl ethylpropanetetracarboxylate boils at 207—212° under a pressure of 25 mm. The less soluble acid forms spherical aggregates of thin, lustrous oblique prisms, and melts at 147—148°; its *silver* salt, $C_8H_9Ag_3O_6$, is a voluminous, white precipitate, very susceptible to the action of light. The more soluble acid was not obtained in sufficient quantity for complete purification.

Propyltricarballylic acid, $COOH{\cdot}CHPr^{\alpha}{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH$, and *isopropyltricarballylic acid*,

$$COOH{\cdot}CHPr^{\beta}{\cdot}CH(COOH){\cdot}CH_2{\cdot}COOH,$$

are readily obtained by heating ethyl fumarate with ethyl propyl- or isopropyl-sodiomalonate. The former crystallises from water on spontaneous evaporation in compact, lustrous prisms which contain water of crystallisation and melt below 100°; when rapidly crystallised, however, it forms nodules consisting of anhydrous plates, melts at 151—152°, and is soluble in alcohol and ether, but almost insoluble in benzene and light petroleum. The mother liquors contain lower melting products which could not be isolated. Isopropyltricarballylic acid crystallises in anhydrous nodules formed of plates or compact prisms, melts at 161—162°, and behaves towards solvents in the same manner as the previous acid.

Determinations of the conductivities of these acids have been made by Walden, and it appears that, as in the case of succinic acid, the introduction of alkyl groups into tricarballylic acid raises the conductivity to a considerable extent.

An attempt was made to bring about the combination of ethyl sodiomalonate and the ethyl salt of Δ^1-tetrahydrophthalic acid, as the latter behaves in many respects as an unsaturated fatty acid.

No reaction, however, was found to take place on digesting the mixture for six hours at 100°. H. G. C.

Furfurylamine. By A. Deutzmann (*Chem. Centr.*, 1891, ii, 295—296; from *Diss. Berlin*).—The following compounds are described:—*Furfurylamine furfuryldithiocarbamate*,

$$C_4OH_3\cdot CH_2\cdot NH\cdot CSSH,NH_2\cdot CH_2\cdot C_4OH_3,$$

is prepared from 6·8 grams of carbon bisulphide dissolved in dry ether and 18 grams of furfurylamine; it is soluble in alcohol, ether, benzene, and light petroleum; when exposed to the air, it becomes yellow. *Furfurylthiocarbimide*, $CS{:}N\cdot CH_2\cdot C_4OH_3$, is prepared from the last-named salt by the action of mercuric chloride, which must not be in excess. *Difurfurylthiocarbamide*, $CS(NH\cdot CH_2\cdot C_4OH_3)_2$, prepared by heating the dithiocarbamate at 100°, melts at 85—86°. *Methylfurfurylthiocarbamide*, prepared from methylthiocarbimide and furfurylamine, melts at 83°. *Ethylfurfurylthiocarbamide* melts at 67°. *Allylfurfurylthiocarbamide* melts at 42—43°. *Phenylfurfurylthiocarbamide* melts at 128°; the *paratolylcarbamide* melts at 165°; the *metaxylylcarbamide* at 121·5°.

Furfurylcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot C_4OH_3$, prepared from furfurylamine and potassium cyanate, melts at 110—111°; *difurfurylcarbamide*, prepared from furfurylamine, potassium hydroxide, and carbonyl chloride dissolved in benzene, melts at 128°. *Ethylfurfurylcarbamide* melts at 95—96°; *amylfurfurylcarbamide* at 120—121°. These were prepared by the aid of ethyl- and amyl-carbimide respectively. *Phenylfurfurylcarbamide* melts at 124°; the *orthotolylcarbamide* at 168—168·5°; the *metaxylylcarbamide* at 178°. From *difurfurylthiocarbamide*, by the action of mercuric oxide, cyanamide and furfurylamine are obtained, but not the corresponding guanidine.

The *hydrochloride of furfurylguanidine*, $C(NH_2)_2{:}N\cdot CH_2\cdot C_4OH_3$, may be prepared by heating cyanamide and furfurylamine hydrochloride at 100° in a sealed tube. Both it and the platinum salt were analysed.

Diphenylfurfurylguanidine, $C(NHPh)_2{:}N\cdot CH_2\cdot C_4OH_3$, is prepared from the last-named compound by heating it with aniline at 80—81°. By treating the amine with methyl iodide, *trimethylfurfurylammonium iodide*, $C_4OH_3\cdot CH_2\cdot NMe_3I$, is obtained.

By distilling furfurylamine hydrochloride, a liquid was obtained which probably contained furfuryl chloride. *Nitrofurfurylamine* is prepared by acting with nitric acid on acetylfurfurylamine in glacial acetic acid, and then distilling with steam. J. W. L.

Intramolecular Change of the Propyl Group. By O. Widman (*J. pr. Chem.* [2], **44**, 414—415; compare Abstr., 1891, 686, 1344).—Fileti (Abstr., 1891, 1344) quotes Widman as having pointed out that the nitration of cumenylacrylic acid produces paranitrocinnamic acid, orthonitroparisopropylcinnamic acid, and an isomeride of the latter which he called orthonitroparapropylcinnamic acid. Widman now points out that Fileti has missed the publications (Abstr., 1891, 69, 45) in which it is shown that this "orthonitroparapropylcinnamic" acid is really a mixture of about one-third metanitro-

cumenylacrylic acid and two-thirds orthonitrocumenylacrylic acid, the mixture having a constant melting point and crystallising in a definite form. A. G. B.

Isomeric Change in the Synthesis of Aromatic Amines and Phenols. By M. Seńkowski (*Ber.*, **24**, 2974—2977).—It is well known that the higher homologues of aniline, produced by heating its alkyl derivatives or the corresponding alcohols with its hydrochloride or stannochloride, invariably belong to the para-series; the same applies to the homologues of phenol obtained by the action of zinc chloride on a mixture of phenol and the alcohol. The experiments to be described were instituted to ascertain whether in these cases intramolecular changes occur similar to those observed in the synthesis of aromatic hydrocarbons by means of aluminium chloride.

Paratertiarybutylphenol (Abstr., 1890, 1296) is obtained by the action of zinc chloride and isobutyl alcohol on phenol in the manner described by A. Liebmann (Abstr., 1882, 171, 727).

Paramidophenyltrimethylmethane (*loc. cit.*, 1890) is formed by heating aniline hydrochloride with isobutyl alcohol in a sealed tube at 230°; it yields trimethylphenylmethane (*loc. cit.*, 1890) by the diazo-reaction.

The so-called isobutylbenzene boiling at 165—170° (Goldschmidt, Abstr., 1882, 952) is a mixture. When treated with bromine in direct sunlight until the colour of the bromine persists for several minutes, and, after washing the product with potash and drying, it is distilled over sodium, a small quantity of a hydrocarbon passes over at 167—168°, apparently identical with trimethylphenylmethane.

Isoamylaniline (Hofmann, this Journal, 1874, 807; Merz and Weith, Abstr., 1882, 179), when treated with one molecular proportion of bromine in sunlight and with a second, in the dark, at the temperature of the water-bath, yields Schramm's isoamylbenzene dibromide melting at 129° (Abstr., 1883, 977), and is, therefore, a normal product. A. R. L.

Action of Nitrous Acid on Resorcinol Diethyl Ether and on Triethylresorcinol. By A. Kraus (*Monatsh.*, **12**, 368—378).—When a solution of resorcinol diethyl ether (1 part) in acetic acid (10 parts) is saturated with hydrogen chloride, and treated in the cold with a large excess of alkaline nitrite, a very considerable quantity of a dark-green precipitate separates. The product is diluted with water and filtered, and the solid thus obtained treated with cold, dilute potash, whereby the greater portion dissolves, forming a dark-red solution, from which hydrochloric acid separates *nitrosoresorcinol ethyl ether*, $NO\cdot C_6H_3(OH)\cdot OEt$, in the form of a voluminous, light-yellow precipitate. The ether may be readily recrystallised from hot water and from hot alcohol (compare Aronheim, *Ber.*, **12**, 30), when it forms thin, pale-yellow scales which decompose at 150° without having previously melted. That part of the above-mentioned product which is insoluble in cold dilute potash is washed with cold alcohol, and dried in a vacuum. On elementary analysis, it gives

numbers corresponding with the formula for *nitrosoresorcinol diethyl ether*, $NO{\cdot}C_6H_3(OEt)_2$. It melts at 122—123°, is soluble in cold chloroform, benzene, and ether, but is decomposed when warmed with those solvents; it has a pale-rose colour, and gives an intense blue coloration with concentrated sulphuric and hydrochloric acids. The *benzoyl derivative* of nitrosoresorcinol ethyl ether, $NO{\cdot}C_6H_3(OEt){\cdot}OBz$, is obtained in the form of yellow flocks on shaking a solution of the ether in soda with an excess of benzoic chloride. When recrystallised from alcohol, it forms beautiful, yellow crystals which melt at 155°.

Nitrosoethylresorcinol ethyl ether, $NO{\cdot}C_6H_2Et(OH){\cdot}OEt$, is obtained when triethylresorcinol (compare Herzig and Zeisel, Abstr., 1890, 1404) is dissolved in ten times its weight of absolute alcohol, and the solution mixed with slightly more than the molecular equivalent of sodium nitrite, and decomposed with concentrated hydrochloric acid until the whole assumes a brownish-yellow colour. On the addition of water, a green, flocculent precipitate is formed, the colour of which gradually changes to reddish-yellow. The precipitate is dissolved in potash, and the solution exhausted with ether; the ethereal extract is acidified, and the yellow precipitate thus obtained crystallised from hot benzene, which furnishes the compound in the form of beautiful, yellow prisms. It dissolves when warmed with ordinary solvents, and decomposes at 150°, without having previously melted; it gives a stable base on treatment with reducing agents, is oxidised by nitric acid, first to a nitro-compound, and eventually to oxalic acid, and forms a well characterised *benzoyl derivative*,

$$NO{\cdot}C_6H_2Et(OEt){\cdot}OBz,$$

which is insoluble in potash, and melts at 141—142°. G. T. M.

Hydroxyquinones. By Kowalski (*Chem. Centr.*, 1891, ii, 377; from *Schweiz. Wochenschr. Pharm.*, **29**, 265).—The author has observed the formation of hydroxyquinones from quinones, when the latter are left exposed to the action of aqueous alkali and air. From α-naphthaquinone and from thymoquinone the corresponding hydroxyquinones were obtained. J. W. L.

Isoeugenol, Diisoeugenol, and their Derivatives. By E. Tiemann (*Ber.*, **24**, 2870—2877).—In his researches on the products of oxidation of acetyleugenol (this vol., p. 59), the author was led to suppose that the eugenol employed might contain a hitherto unknown isomeride, or that such a compound might be formed as an intermediate product during its oxidation. He therefore examined the action of various reagents on eugenol, but only succeeded in converting it into the already known isomeride, isoeugenol,

$$CHMe{:}CH{\cdot}C_6H_3(OMe){\cdot}OH\ [1:3:4].$$

This molecular interchange proceeds best when carried out as follows:—12·5 parts of potash are dissolved in 18 parts of amyl alcohol, 5 parts of eugenol added, the mixture heated for 16—20

hours at 140°, and the amyl alcohol removed by distillation in a current of steam. Sulphuric acid is then added, the isoeugenol separated, washed with sodium carbonate solution, and distilled in a current of steam. It then boils at 261° (uncorr.), and has all the properties assigned to it by Kraaz and Tiemann (Abstr., 1883, 201); in alcoholic solution, it is coloured olive-green by ferric chloride, and if left it becomes yellow, but much less rapidly than eugenol. Its coefficient of refraction is 1·5728, that of eugenol being 1·5438.

The substance described by Kraaz and Tiemann as benzoylisoeugenol is in reality a derivative of diisoeugenol, and not of isoeugenol. The monomolecular acetyl and benzoyl compounds can only be obtained under certain conditions. *Acetylisoeugenol*, $C_{10}H_{11}O_2Ac$, is prepared by boiling the phenol with acetic anhydride, and separates in lustrous, white needles on the addition of light petroleum to its benzene solution; it melts at 79—80°, boils at 282—283° (uncorr.), and is reconverted into isoeugenol by alkalis. *Benzoylisoeugenol*, $C_{10}H_{11}O_2Bz$, is formed by the action of benzoic chloride on a solution of isoeugenol in dilute soda, provided the liquid never becomes acid; it crystallises from alcohol in white prisms melting at 103—104°.

Diacetyldiisoeugenol, $C_{20}H_{22}O_4Ac_2$, is obtained by adding acetyl chloride to isoeugenol previously warmed to 54°, and raising the temperature to 80°, heating as long as hydrogen chloride is evolved. The product solidifies on cooling, and may be separated from adhering oil by means of ether; the residue is crystallised from boiling alcohol, and then forms white needles which melt at 150—151°, and are almost insoluble in water and ether. *Dibenzoyldiisoeugenol*, $C_{20}H_{22}O_4Bz_2$, is the compound previously described by Kraaz and Tiemann (*loc. cit.*) as benzoylisoeugenol. Both these substances on hydrolysis yield *diisoeugenol*, which may also be obtained by the action of mineral acids or acid salts on isoeugenol; it crystallises from 50 per cent. alcohol in slender needles, melts at 180—181°, is readily soluble in ether and chloroform, less easily in alcohol, and almost insoluble in water and light petroleum. Its alcoholic solution is coloured olive-green by ferric chloride.

The molecular weight of diisoeugenol, as found by Raoult's method, agrees with the above formula, but no evidence as to its constitution has yet been obtained. It might possibly be a tetramethylene derivative of a formula such as

$$\begin{array}{l} CHMe\cdot CH\cdot C_6H_3(OMe)\cdot OH \\ | \qquad\quad | \\ CHMe\cdot CH\cdot C_6H_3(OMe)\cdot OH' \end{array}$$

or it may be a diphenyl derivative. Further investigation of this compound is in progress. H. G. C.

Oxidation Products of Safrole. By F. Tiemann (*Ber.*, **24**, 2879—2886).—The results given in the preceding abstract and on p 59 show that acetyleugenol and acetylisoeugenol are compounds which readily undergo decomposition, and that in their oxidation several processes occur simultaneously; the exact investigation of these processes has been rendered still more difficult by the fact that in the secondary reactions the benzene nucleus itself has been attacked. The author

therefore wished to follow out the oxidation processes in a phenyl-allylene derivative, in which the action of the oxidising agent would be confined to the carbon side chain. Such a derivative has been found in safrole, which has been shown by Eykman (Abstr., 1886, 95) and Poleck (Abstr., 1884, 1339; 1886, 697) to have the constitution $CH_2<^{O\ (3)}_{O\ (4)}>C_6H_3\cdot CH_2\cdot CN{:}CH_2$ (1).

On carefully oxidising safrole with $1\frac{1}{2}$ per cent. permanganate solution at 70—80°, it takes up two hydroxyl groups, forming *methylene-3 : 4-dihydroxybenzyl glycol*, $CH_2<^{O}_{O}>C_6H_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, which crystallises from benzene in white needles, melts at 82—83°, and is readily soluble in boiling water and ether, less easily in alcohol. Its *diacetate*, $C_{10}H_{10}O_4Ac_2$, is a pale-yellow oil boiling at 240° under a pressure of 15—20 mm.; and the *diphenylcarbamate*,

$$C_{10}H_{10}O_4(CO\cdot NHPh)_2,$$

obtained by the action of phenyl isocyanate on the glycol, crystallises in plates, and melts at 127°.

If 5 parts of safrole be warmed at 70—80° with 12·5 parts of permanganate, 5 parts of acetic acid, and 1000 parts of water, piperonal, piperonic acid, and α-homopiperonic acid are obtained. The first is removed by extracting the alkaline solution with ether, and the alkaline solution is then concentrated, acidified, and extracted with ether. The residue obtained from this extract, which contains piperonic and α-homopiperonic acids, is boiled with magnesium carbonate, resinous matters being removed by ether, the solution again acidified and taken up with ether, the latter evaporated, and the residual mixture of the two acids separated by fractional crystallisation from hot water.

α-Homopiperonic acid, $CH_2<^{O}_{O}>C_6H_3\cdot CH_2\cdot COOH$, crystallises in white needles, melts at 127—128°, and dissolves readily in boiling water, alcohol, ether, and hot benzene, scarcely at all in light petroleum. The *calcium* salt contains 2 mols. H_2O, which are given off at 100°; the *copper* salt, $(C_9H_7O_4)_2Cu$, forms a pale-green, crystalline powder; the *silver* salt, $C_9H_7O_4Ag$, a white, crystalline powder, which may be crystallised from hot water; the *zinc* salt, $(C_9H_7O_4)_2Zn$, is also white and crystalline. The *methyl* salt, $C_9H_7O_4Me$, and *ethyl* salt, $C_9H_7O_4Et$, are yellow oils boiling at 278—280° and 291° respectively, and the *amide*, $C_8H_7O_3\cdot CON\,H_2$, crystallises in needles melting at 172—173°. On treatment with nitric acid, α-homopiperonic acid yields a *nitro-compound*, $C_9H_7O_4\cdot NO_2$, which crystallises in yellow plates, and melts at 188°. Further oxidation converts the acid into piperonic acid and piperonal.

From these results, it appears that the allenyl group of safrole undergoes oxidation in a normal manner; the intermediate homopiperonal, $CH_2<^{O}_{O}>C_6H_3\cdot CH_2\cdot CHO$, has not been isolated, owing probably to its instability; so far also no indication of a compound corresponding with acetovanillone has been observed. H. G. C.

Action of Benzyl Chloride on Orthotoluidine. By C. Rabaut (*Bull. Soc. Chim.* [3], **5**, 742—743).—*Benzylorthotoluidine*, $C_6H_4Me{\cdot}NHPh$, is formed when benzyl chloride (1 mol.) is heated with orthotoluidine (2 mols.) in an open vessel for 40 hours at 175°. The crystalline product of the reaction is treated with aqueous sodium carbonate, and yields a dark, chestnut-coloured oil, which, on purification, becomes almost colourless. Benzylorthotoluidine boils at 210° under a pressure of 25 mm., crystallises from alcohol in tufts, melts at 56—57°, and is soluble in the ordinary menstrua. The *hydrochloride* forms white crystals, is soluble in alcohol and hot water, and unites with platinum chloride to form a yellow, crystalline *platinochloride*. The *acetate*, *sulphate*, *nitrate*, and *oxalate* are white.

When benzylorthotoluidine is treated with ethyl iodide, benzylethylorthotoluidine, $C_6H_4Me{\cdot}NEt{\cdot}CH_2Ph$, is obtained as a yellowish, neutral oil boiling at 230° under 25 mm. pressure.

Acetylbenzylorthotoluidine is solid at ordinary temperatures, and boils at 280—285° under a pressure of 20 mm. Jn. W.

Oxidation of Azo-compounds. By C. Lauth (*Compt. rend.*, **112**, 1512—1514).—Azo-compounds, when oxidised by various reagents in the cold, yield diazo-compounds together with quinones. Acid and alkaline reagents give similar results; the author has chiefly employed lead dioxide in the presence of sulphuric acid.

The sodium salt of benzeneazo-β-naphtholdisulphonic acid is dissolved in 30 parts of water; to the solution, 2 parts of sulphuric acid (66°) and 1 part of the lead dioxide are added; the red-orange solution rapidly becomes lemon-yellow, and there is no evolution of gas in the cold. Nitrogen is rapidly evolved on heating, and, when distilled, phenol comes over in the first portions of the distillate. The diazo-solution, on treatment with an alkaline solution of phenol, phenolsulphonates, or amines, gives azo-colouring matters; for example, the addition of β-naphtholdisulphonic acid regenerates benzene-azo-β-naphtholdisulphonic acid. Compounds substituted in the diazo-group react equally well: Orange I (the sodium salt of sulphobenzeneazo-α-naphthol) yields, similarly, a diazo-solution, giving, on distillation, phenylparasulphonic acid. Again, sulphobenzeneazo-phenol, by oxidation, yields a diazo-solution, which, on the addition of an alkaline solution of α-naphthol, gives Orange I.

The reaction has been applied to a large number of azo-compounds, including unsubstituted compounds, such as azobenzene, as well as compounds containing amido-, hydroxy-, or carboxyl-groups. No exception has been found to the general course of the reaction indicated above. The reaction may be considered to be characteristic of the azo-compounds.

When the liquid, after oxidation, is filtered from the lead sulphate formed, it yields a quinone in the case of sulphobenzeneazo-phenol; in other cases the residue contains most of the oxidation products.

The general reaction for the oxidation is of the type of

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + H_2SO_4 + O_2 = C_6H_5{\cdot}N_2{\cdot}SO_4H + C_{10}H_6O_2 + H_2O.$$

intermediate products may be obtained at the same time, if the oxidising agent is not present in sufficient quantity, as well as tetrazo-compounds. W. T.

Action of Phenylhydrazine on Phenols. By A. Seyewetz (*Compt. rend.*, **113**, 264—267).—Phenol, the cresols, and the naphthols do not yield compounds with phenylhydrazine in presence of various solvents, and under various conditions.

Dihydric phenols behave differently, and readily combine with phenylhydrazine, the reaction being so distinct in the case of orcinol that it would almost seem to indicate the presence of a ketonic or aldehydic group in this compound.

A concentrated aqueous solution of the phenol is mixed with a solution of phenylhydrazine in water slightly acidified with acetic acid. After agitating for some minutes, the compound separates, is washed with water containing a little acetic acid, and then recrystallised from benzene.

Quinol yields the compound $C_6H_4(OH)_2,2NHPh{\cdot}NH_2$, which crystallises from boiling benzene in small, white, nacreous plates melting at 70—71°. It gradually alters when exposed to the air, and becomes yellow, is slightly soluble in cold water, somewhat soluble in warm water, alcohol, chloroform, ether, and benzene, very slightly soluble in light petroleum. Alkalis liberate phenylhydrazine, even in the cold; acids liberate the phenol.

Resorcinol yields the compound described by Baeyer and Kochendoerfer.

Orcinol readily yields the compound $C_6H_3Me(OH)_2,2NHPh{\cdot}NH_2$, which forms white crystals melting at 61—62°, and similar in general properties to the quinol derivative.

Catechol seems not to form a corresponding compound, and this is true also of pyrogallol.

Salicylic acid, in presence of toluene, yields a compound crystallising in slender, white needles, and melting at 122—123°. In many cases, however, the finding of a suitable solvent constitutes a great difficulty. C. H. B.

Combination of Phenylhydrazine with Ethyl Oxalacetate. By W. Wislicenus and M. Scheidt (*Ber.*, **24**, 3006—3010).—On mixing together ethereal solutions of phenylhydrazine and ethyl oxalacetate in molecular proportion, and cooling, an additive compound is deposited in colourless, lustrous plates; it may be crystallised from absolute alcohol, and melts at 105—106°. This substance is distinguished from the hydrazone (m. p. 76—78°) by its colour, and by its insolubility in ether and in light petroleum. The additive compound is readily converted into the hydrazone by fusion, or by heating it in solution; at ordinary temperatures the change is more gradual. The constitution of this compound may be represented by the formula $COOEt{\cdot}C(OH)(NH{\cdot}NHPh)CH_2{\cdot}COOEt$, which would readily explain its conversion into the hydrazone; from the general properties of the substance, however, as well as from the fact that all efforts hitherto made to prepare similar substances from other

less acid, ketonic, ethereal salts have failed, the authors consider it to be an analogue of the ammonium salts, with the formula $COOEt{\cdot}CO{\cdot}CH(NH_3{\cdot}NHPh){\cdot}COOEt$ or

$$COOEt{\cdot}C(O{\cdot}NH_3{\cdot}NHPh){:}CH{\cdot}COOEt.$$

The same substance is also formed by the action of phenylhydrazine hydrochloride on ethyl sodoxalacetate in cold, concentrated, aqueous solution.

Methyl oxalacetate and ethyl ethoxyoxalacetate yield additive compounds with phenylhydrazine similar to the one described above, whilst ethyl methyloxalacetate, ethyl oxalsuccinate, ethyl acetoacetate, ethyl benzoylacetate, and ethyl levulinate do not react in this manner.

J. B. T.

Oximes and so-called Stereochemistry. By A. Claus (*J. pr. Chem.* [2], **44**, 312—335).—This paper deals with the isomerism of the hydroxylamine derivatives of benzile, and especially with the recent work of Auwers and Meyer on the subject (Abstr., 1889, 403, 609, 611, 713). The author concludes by claiming that he has incontrovertibly proved that all manifestations of isomerism among the products of the reaction of hydroxylamine with benzile can be efficiently and easily explained as cases of isomerism in structure, without having recourse to any stereochemical hypothesis.

A. G. B.

Intramolecular Change of some Isoaldoxime Derivatives. By R. Behrend (*Annalen*, **265**, 238—246).—When pure benzylisoparanitrobenzaldoxime (m. p. 118°) is dissolved in alcohol (9—10 parts), and the solution warmed with a few drops of a dilute alcoholic solution of sodium ethoxide, it is partially converted into paranitrobenzylisobenzaldoxime; this change is expressed by the equation

$$NO_2{\cdot}C_6H_4{\cdot}CH{<}\overset{O}{\underset{}{}}{>}N{\cdot}CH_2Ph = NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{<}\overset{O}{\underset{}{}}{>}CHPh,$$

and is, to a certain extent, reversible, as when paranitrobenzylisobenzaldoxime is treated with sodium ethoxide under the same conditions, it is in part transformed into benzylisoparanitrobenzaldoxime.

When benzylisometanitrobenzaldoxime, prepared by the condensation of metanitrobenzaldehyde with β benzylhydroxylamine, is warmed with a dilute alcoholic solution of sodium ethoxide, it is partially converted into the isomeric metanitrobenzylisobenzaldoxime, and on evaporating the solution, a mixture of the two isomerides is left; this is dissolved in alcohol (about 10 parts), and on keeping the solution for about 24 hours, the greater part of the unchanged benzylisonitrobenzaldoxime is deposited in crystals, whilst most of the isomeride remains in solution; the latter is obtained in a pure condition by repeated fractional crystallisation from alcohol.

Metanitrobenzylisobenzaldoxime, $C_{14}H_{12}N_2O_3$, purified in the manner just described, crystallises from hot alcohol and benzene, in both of

which it is readily soluble, in lustrous, pale-yellow needles, melts at 114—115°, and is only sparingly soluble in ether, and almost insoluble in light petroleum. It seems to be unchanged by a warm solution of sodium ethoxide, but when heated with hydrochloric acid, it is decomposed into benzaldehyde and *β-metanitrobenzylhydroxylamine hydrochloride;* the latter is readily soluble in water, but more sparingly in alcohol, from which it is precipitated on the addition of ether, as a colourless, crystalline powder, melting at 145—146°, with previous softening; the melting point of the salt which has once been melted is much higher. The free *base* crystallises from hot water in needles, melts at 79·5—80·5°, and reduces Fehling's solution.

Benzylisoanisaldoxime is not acted on by sodium ethoxide under the conditions described above. F. S. K.

Amidines. By W. Lossen (*Annalen*, **265**, 129—178).—The interesting results obtained on treating benzenylamidine and other amidines with nitrous acid (Abstr., 1891, 1038—1042) have led the author and his pupils (Mierau, Kobbert, Neubert, C. Lossen, Kirschnick, and Grabowski) to subject the amidines to a somewhat extended investigation, in order to determine (1) which of these compounds form dioxytetrazotic acids and stable nitrites, and (2) how the properties of the amidines compare with those of the amidoximes.

Benzenylamidine sulphate, $(C_7H_8N_2)_2,H_2SO_4 + H_2O$, is easily obtained by evaporating a solution of the nitrite with the theoretical quantity of sulphuric acid, and extracting the residue with alcohol and ether successively; the insoluble sulphate is then dissolved in water and reprecipitated by the addition of alcohol; it loses its water at 80—81°, and decomposes into benzonitrile and ammonium sulphate on further heating. The *formate*, $C_7H_8N_2,CH_2O_2 + H_2O$, prepared by decomposing the sulphate with barium formate, crystallises well, is readily soluble in alcohol and water, and loses its water over sulphuric acid. The *acetate*, $C_7H_8N_2,C_2H_4O_2$, forms monoclinic crystals, $a : b : c = 1·099 : 1 : ?$, $\beta = 120° 13'$, and is readily soluble in water and alcohol. The *nitrite*, $C_7H_8N_2,HNO_2 + H_2O$, can be obtained by evaporating a solution of equivalent quantities of benzenylamidine hydrochloride and sodium nitrite; it crystallises from alcohol in monoclinic (or rhombic ?) plates, $a : b : c = 3·467 : 1 : 3·425$, $\beta = 94° 32'$, and decomposes below 70° with formation of benzonitrile; it is readily soluble in water and alcohol, but insoluble in ether.

Phenylbenzenylamidine can be prepared by triturating benzimidoethyl ether hydrochloride (1 mol.) with warm aniline (1 mol.), and also by treating benzanilide imidochloride with anhydrous ammonia in light petroleum solution; it melts at 112°, and is identical with the compound obtained by Bernthsen (*Annalen*, **184**, 348; **192**, 29) by treating aniline hydrochloride with thiobenzamide, or with benzonitrile; its constitution is probably expressed by the formula $NH_2·CPh:NPh$. When this amidine is treated with nitrous acid under various conditions, it yields benzanilide as the sole product, a fact which shows that the nitrite of the base is very unstable.

Phenylbenzimidoethyl ether, NPh:CPh·OEt, is formed in preparing phenylbenzenylamidine by the action of aniline on benzimidoethyl ether hydrochloride; it is an oily liquid, the hydrochloride of which decomposes at about 60° into benzanilide and ethyl chloride. When the oil is heated at about 70° with phosphorus pentachloride, it undergoes decomposition into ethyl chloride and benzanilideimido chloride, CClPh:NPh.

Metanitrobenzimidoethyl ether hydrochloride, identical with the compound described by Tafel and Enoch (Abstr., 1890, 973), can be prepared by passing hydrogen chloride into a well-cooled, alcoholic benzene solution of metanitrobenzonitrile; the *platinochloride*,

$$(C_9H_{10}N_2O_3)_2,H_2PtCl_6,$$

is a reddish-yellow compound.

When metanitrobenzimidoethyl ether hydrochloride is treated with alcoholic ammonia, it is converted into metanitrobenzenylamidine hydrochloride (compare Tafel and Enoch, *loc. cit.*). The corresponding *sulphate*, $[NO_2·C_6H_4·C(NH_2):NH]_2,H_2SO_4$, prepared from the nitrite, is soluble in water and alcohol. The *nitrite*,

$$NO_2·C_6H_4·C(NH_2):NH,HNO_2,$$

is obtained when a concentrated solution of the hydrochloride is treated with silver nitrite, and the filtrate evaporated at 30—40°; it crystallises in prisms, and decomposes when heated, yielding metanitrobenzonitrile, water, and nitrogen.

Metanitrobenzoylbenzamide, $NO_2·C_6H_4·CO·NH·COPh$, is formed when metanitrobenzenylamidine is treated with benzoic chloride and potash; it crystallises from alcohol in plates, and melts at 133—134°. An *ethyl* derivative of metanitrobenzenylamidine can be obtained by treating the amidine with ethyl iodide in ethereal solution; its *platinochloride* has the composition $(NO_2·C_6H_4·N_2H_2Et)_2,H_2PtCl_6$. When metanitrobenzenylamidine is treated with hydroxylamine, it is converted into the corresponding amidoxime.

Phenylmetanitrobenzimido ether, $NO_2·C_6H_4·C(:NPh)·OH$, is formed, together with phenylmetanitrobenzenylamidine, when metanitrobenzimido ether hydrochloride is warmed with aniline; it crystallises in yellow prisms, melts at 55—56°, and is readily soluble in cold hydrochloric acid; when heated with alcoholic ammonia at 100°, it is decomposed into aniline and metanitrobenzonitrile.

Phenylmetanitrobenzenylamidine, $NO_2·C_6H_4·C(:NPh)·NH_2 + H_2O$, can also be obtained by heating metanitrobenzonitrile with aniline hydrochloride; it crystallises from ether in yellow prisms, melts at 72—73°, and decomposes at 100°. The *hydrochloride*,

$$NO_2·C_6H_4·CN_2H_2Ph,HCl,$$

melts at about 251°. When an ethereal solution of the amidine is heated at 100° with ethyl iodide, a yellow, crystalline salt of the composition $NO_2·C_6H_4·CN_2HPhEt,HI$ is formed.

Symmetrical diphenylbenzenylamidine is not acted on by nitrous acid; when anhydrous asymmetrical diphenylbenzenylamidine is warmed with amyl nitrite, or treated with nitrous acid in aqueous solution, it is converted into diphenylbenzamide (m. p. 175°).

Ethylbenzenylamidine, CN_2H_2PhEt, is formed when benzimido ether hydrochloride is treated with a 25 per cent. solution of ethylamine, but it cannot be obtained in a pure condition. The *hydrochloride*, CN_2H_2PhEt,HCl, crystallises from alcoholic ether in needles, melts at 161°, and decomposes above 200° with formation of benzonitrile and ethylamine hydrochloride; it is very readily soluble in water and alcohol. The *platinochloride*, $(CN_2H_2PhEt)_2,H_2PtCl_6$, crystallises from alcohol in microscopic, reddish-yellow prisms. The *nitrate*,

$$CN_2H_2PhEt,HNO_3,$$

is deposited in long needles when a solution of the nitrite in fuming nitric acid is evaporated at the ordinary temperature; it is very readily soluble in water. The *nitrite*, CN_2H_2PhEt,HNO_2, prepared by treating an aqueous solution of the hydrochloride with silver nitrite, crystallises from alcohol in slender needles, melts at 122°, and is very readily soluble in water and alcohol, but almost insoluble in ether; it is only slowly decomposed by boiling water, and it is stable in presence of nitrous acid. The *benzoyl* derivative, $C_{16}H_{16}N_2O$, crystallises from dilute alcohol in needles, melts at 88°, and is only moderately easily soluble in ether. The *diethyl* derivative is formed when the amidine is heated at 100—110° with an ethereal solution of ethyl iodide; its *hydriodide*, $C_{11}H_{16}N_2,HI$, is a colourless, crystalline compound, but turns yellow on keeping.

Acetamidine nitrite, CN_2H_3Me,HNO_2, prepared by treating a concentrated aqueous solution of acetamidine hydrochloride with silver nitrite, melts at 148° with decomposition, and is soluble in water and alcohol, but insoluble in ether.

Propionamidine nitrite, CN_2H_3Et,HNO_2, obtained in like manner, separates from alcohol in crystals, melts at 116°, and is readily soluble in water and alcohol.

Paratolenylamidine nitrite, $C_6H_4Me{\cdot}CN_2H_3,HNO_2$, crystallises in needles, melts at 133°, and is readily soluble in alcohol and water, but insoluble in ether.

Isophthalamidine nitrite, $C_6H_4(CN_2H_3)_2,2HNO_2$, crystallises from water in lustrous needles.

Succinimidine nitrite, $C_2H_4<\begin{matrix}C(NH)\\C(NH)\end{matrix}>NH,HNO_2 + \frac{1}{2}H_2O$, is formed when a solution of a mixture of the hydrochlorides of succinamidine and succinimidine is treated with silver nitrite; it crystallises in small, yellow plates.

Guanidine nitrite, CH_5N_3,HNO_2, can be obtained by evaporating a solution of guanidine sulphate with sodium nitrite, and extracting the residue with alcohol, from which the nitrite is deposited in crystals; it melts at 76—78·5°, decomposes at about 120°, and is readily soluble in water and alcohol, but insoluble in ether.

From the results of the experiments described above, the author concludes that the substituted amidines cannot be converted into dioxytetrazotic acids. The strongly basic amidines combine unchanged with nitrous acid, but when, by the substitution of a phenyl group for hydrogen, they are converted into feeble bases, they become less stable towards nitrous acid. F. S. K.

Thio-derivatives of Orthamidobenzamide. By A. Stewart (*J. pr. Chem.* [2], **44**, 415—416).—The *compound* $C_{11}H_{10}N_2SO$ is obtained by heating orthamidobenzamide with allylthiocarbamide (equivalent proportions) in benzene for several hours. It crystallises from hot alcohol, ether, or benzene in colourless needles and tables, and melts with decomposition at 198—199°. It dissolves in alkalis, and is reprecipitated by acids unchanged; its solution in benzene has a blue fluorescence.

A compound which crystallises in colourless, silky tables is formed when phenylthiocarbimide is substituted for the allyl compound in the above reaction.

By heating orthamidobenzamide with thiocarbamide in an oil-bath at 180—200°, until no more ammonium sulphide is given off, the *compound* $C_8H_6N_2SO$ is formed; it crystallises from alcohol in creamy-white nodules, dissolves in ether and benzene, and melts at 280—281°. It dissolves in alkalis, and is reprecipitated by acids. When heated for 2—3 hours with methyl iodide (2 mols.) and sodium (2 mols.) in a tube at about 130°, a smell of mercaptan is perceived, and beautiful, colourless, six-sided prisms crystallise out; they contain sulphur, dissolve in alkalis, and are unchanged at 300°.

A colourless, crystalline substance is obtained when thiocarbamide is heated with anthranilic acid.

The author suggests constitutional formulæ for some of the above compounds, but does not support them. The investigation is proceeding. A. G. B.

Condensation of Anilpyruvic Acid. By C. Böttinger (*Annalen*, **265**, 253—256).—In the conversion of anilpyruvic acid into aniluvitonic acid by treatment with concentrated sulphuric acid, a very small quantity of a compound, which is insoluble in alkalis, is formed; this substance has the composition $C_{17}H_{16}N_2O$, melts at 194—195°, and is identical with the compound obtained by Lazarus by treating aniline with pyruvic acid at a high temperature. The condensation product of paratoluidine and pyruvic acid has consequently the composition $C_{19}H_{20}N_2O$, and not $C_{16}H_{20}N_2O$, as given by Lazarus. F. S. K.

Tartranilide. By H. Polikier (*Ber.*, **24**, 2959—2962).—Tartranilide is obtained in almost theoretical yield by gradually adding tartaric acid (1 part) to boiling aniline (5 parts), and after a time distilling off the excess of aniline from the solution, washing the solid residue successively with dilute hydrochloric acid, boiling water, and a little alcohol, and finally crystallising from alcohol; it melts above 250° with decomposition. The *diacetyl derivative*,

$$C_2H_2(OAc)_2(CO\cdot NHPh)_2,$$

is formed when tartranilide is boiled in a reflux apparatus with acetic anhydride until the solution commences to darken; it crystallises in needles, melts at 227°, and is more soluble in alcohol, ether, and chloroform than tartranilide. The *triacetyl derivative*, $C_{22}H_{22}O_7N_2$, is

produced by heating tartranilide with acetic anhydride in a sealed tube at 150° for two hours; it forms delicate, lustrous, white needles, melts at 216°, and is readily soluble in alcohol, ether, and glacial acetic acid. The *tetracetyl derivative*, $C_2H_2(OAc)_2(CO{\cdot}NAcPh)_2$, is obtained when tartranilide (3 grams) is heated with acetic chloride (5 grams) in a sealed tube at 140° for two hours, the product being washed with a little glacial acetic acid, and repeatedly crystallised from alcohol; it forms colourless needles, melts at 137°, and is more easily soluble in all solvents than the di- and tri-derivatives.

When tartranilide is submitted to dry distillation, or better, when a mixture of tartaric acid (1 part) and aniline (4 parts) is heated for half an hour at the boiling point of aniline, then distilled over a free flame until nothing but a carbonaceous mass remains, the distillate again treated with tartaric acid, and the same operation repeated several times, on adding dilute hydrochloric acid to the last distillate, dianilidosuccinanilide, $C_2H_2(NHPh)_2(CO{\cdot}NHPh)_2$, melting at 220°, is precipitated, the yield being at most 20 per cent. It is very stable, being attacked neither by acids nor alkalis, and boiling at about 300°. The *acetyl derivative*,

$$NPhAc{\cdot}CH(CO{\cdot}NHPh){\cdot}CH(NHPh){\cdot}CO{\cdot}NHPh,$$

is prepared by boiling dianilidosuccinanilide with acetic anhydride in a reflux apparatus for two hours; it crystallises in large, yellow leaves, and melts at 252°. A. R. L.

Aromatic Dithiocarbamates. By S. M. Losanitsch (*Ber.*, **24**, 3021—3028).—Ammonium phenyldithiocarbamate, $NHPh{\cdot}CS{\cdot}SNH_4$, is prepared by the interaction of aniline, carbon bisulphide, and ammonia or ammonium sulphide, in dilute alcoholic solution at ordinary temperatures; it crystallises in large, yellow, transparent prisms, and is soluble in aqueous ammonia or ammonium sulphide, but decomposes when dissolved in alcohol or water. Ammonium sulphide, ammonium thiocarbonate, carbon bisulphide, thiocarbanilide, and aniline are formed on heating the compound at 100°. Ammonium phenyldithiocarbamate appears to be identical with the "phenylammonium thiouramate" of Hlasiwetz and Kachler.

Phenyldithiocarbamic thioanhydride, $(CS{\cdot}NHPh)_2S$, is obtained by the action of iodine in excess on ammonium phenyldithiocarbamate: it crystallises from benzene in yellow, lustrous needles, melts at 136—138°, and is not affected by acids, but is converted into thiocarbanilide on treatment with potash. *Barium phenyldithiocarbamate*, $(NHPh{\cdot}CSS)_2Ba$, is insoluble in alcohol or water at ordinary temperatures, and crystallises in yellow plates. The *potassium salt*, $NHPh{\cdot}CSSK$, is deposited in long, thin, colourless needles; the *nickel* salt forms yellow, lustrous plates. The remaining salts are sparingly soluble, and on heating are decomposed quantitatively into the metallic sulphide and phenylthiocarbimide.

Methyl phenyldithiocarbamate, $NHPh{\cdot}CSSMe$, prepared from methyl iodide and ammonium phenyldithiocarbamate, crystallises from alcohol in large, white needles; it melts at 93·5°, not at 87—88°, as stated by Will. The *ethyl salt* melts at 59·5°.

By the interaction of carbon bisulphide, aniline, and tetramethylammonium hydroxide in alcoholic solution, a compound is obtained which crystallises in yellow needles and melts at 152—153°; this substance is not a phenyldithiocarbamate, and is being further investigated.

Ammonium paratoluyldithiocarbamate, $C_6H_4Me\cdot NH\cdot CS\cdot SNH_4$, is prepared in a similar manner to the phenyl derivative, and crystallises in large, yellow prisms. The *barium* salt is deposited in colourless needles; the *nickel* salt forms brown needles. The observations of Will and Bilschowski on the methyl and ethyl salts of the above compound are confirmed.

Barium metatoluyldithiocarbamate resembles the para-compound; it is soluble in water, but not in alcohol. The *nickel* salt crystallises in yellowish-brown, lustrous plates. The *methyl* salt,

$$C_6H_4Me\cdot NH\cdot CSSMe,$$

crystallises from alcohol in colourless needles, and melts at 89°.

Barium orthotoluyldithiocarbamate is obtained in colourless plates, which are insoluble in water or alcohol; the *nickel salt* forms brown needles. The *methyl* salt crystallises from alcohol in colourless needles, and melts at 132°.

Barium α-naphthyldithiocarbamate is prepared in a manner similar to the preceding compounds, and is deposited in colourless, insoluble needles; the *nickel salt* crystallises in yellowish-brown needles.

Barium β-naphthyldithiocarbamate forms yellow, crystalline plates; the *nickel salt* resembles that of the α-derivative.

The difference in behaviour between aliphatic and aromatic amines towards carbon bisulphide appears to be due to the extremely feeble basic properties of the aromatic ammonium group (NH_3X), since, in presence of a base, the aromatic amines react in a manner similar to the aliphatic amines, yielding dithiocarbamates. J. B. T.

Ethyl Acetoacetate Aldehydeuramides. By P. Biginelli (*Ber.*, **24**, 2962—2967; compare Abstr., 1891, 908).—When salicyldiureïde (Schiff, *Annalen*, **151**, 199) which has been previously dehydrated, first in a vacuum, and then by heating at 90—100°, is boiled with absolute alcohol and ethyl acetoacetate (2 mols.), ethyl β-uramidocrotonate, and a substance having the composition $C_{14}H_{16}N_2O_4$, are obtained; the latter is also formed when carbamide, salicylaldehyde, and ethyl acetoacetate are boiled together, in molecular proportion, with a little alcohol; it appears to be a mixture of two isomerides, and separates from alcohol in small needles melting at 199—200°, and large prisms melting at 203—204°, these having probably the constitutions $OH\cdot C_6H_4\cdot CH{:}N\cdot CO\cdot N{:}CMe\cdot CH_2\cdot COOEt$ and

$$OH\cdot C_6H_4\cdot CH{:}N\cdot CO\cdot NH\cdot CMe\cdot CH\cdot COOEt$$

respectively. If the prisms are dissolved in hot alcohol, the needles separate out on cooling, whereas if the latter are allowed to remain in contact with this solvent they change by degrees into the former. The substance is insoluble in water, and decomposes when boiled with it; it,

however, dissolves in dilute potassium hydroxide, but the solution becomes yellow after a time, owing to decomposition. When a current of carbonic anhydride is passed through the alkaline solution until the substance commences to separate out, hydrochloric acid precipitates the compound $C_{11}H_{12}N_2O_2$, which crystallises from alcohol in white needles, decomposes at 260—270° without melting, and is insoluble in alkalis; it probably has the constitution $CHMe<\begin{matrix}NH\cdot CO\cdot N:CH\\ CH_2--O--C_6H_4\end{matrix}$; it is formed more readily from the isomeride of lower melting point.

Cumindiureïde, $C_6H_4Pr^{\beta}\cdot CH(NH\cdot CO\cdot NH_2)_2$, is prepared by adding sufficient alcohol to a concentrated aqueous solution of carbamide to enable it to dissolve cumaldehyde, allowing the mixture to remain for two days, collecting the precipitated compound, drying, and washing with ether; it is a colourless, crystalline powder, insoluble in water, only slightly soluble in boiling alcohol, and melts at 175—176°. The compound $C_{17}H_{22}N_2O_3$ is obtained when a solution of cumindiureïde and ethyl acetoacetate in absolute alcohol, or one of carbamide, cumaldehyde, and ethyl acetoacetate in the same solvent is boiled; it crystallises from alcohol in delicate needles, and melts at 161—162°; if left for some days in contact with the solvent, or if repeatedly fused, it changes its form to octahedra, and then melts at 164—165°.

Cinnamdiureïde, $CHPh:CH\cdot CH(NH\cdot CO\cdot NH_2)_2$, separates as a white, crystalline substance, when a concentrated aqueous solution of carbamide is shaken with cinnamaldehyde; it melts at 172° with decomposition.

Tricinnamtetraureïde, $C_9H_8(NH\cdot CO\cdot NH\cdot C_9H_8\cdot NH\cdot CO\cdot NH_2)_2$, is obtained by gently heating a solution of carbamide and cinnamaldehyde in alcohol; it is a yellowish powder, and melts at 183—184° with decomposition. Both ureïdes are decomposed on boiling with water, or more quickly by dilute acids; nitrous acid occasions complete decomposition, and when suspended in ether they absorb bromine. When cinnamaldehyde is shaken with a very dilute solution of carbamide at a moderate temperature for a long time, a ureïde melting at 212° is formed; but if an excess of cinnamaldehyde is digested with a concentrated solution of carbamide at 50—60° for an hour, a ureïde melting at 115—116° is produced. When either of the cinnamureïdes is heated with ethyl acetoacetate, the *compound* $C_{16}H_{18}N_2O_3$, crystallising from alcohol in needles, and melting at 243—244°, is obtained; this appears also to exist in two forms, the melting points of which are very close. Although, as Schiff has shown, furfuraldehyde does not yield a ureïde, when this aldehyde is heated with carbamide and ethyl acetoacetate, *ethyl β-furfuramidocrotonate*, $C_4OH_3\cdot CH:N\cdot CO\cdot NH\cdot CMe:CH\cdot COOEt$, is formed. When the benzuramide derivative (m. p. 207—208°; Abstr., 1891, 908) is crystallised from hot alcohol, needles are obtained having the melting point 206—206·5°. A. R. L.

Ethylation of Salicylaldehyde. By M. Löw (*Monatsh.*, **12**, 393—401).—The author has ethylated salicylaldehyde by slowly

adding a mixture of it (1 mol.) with ethyl iodide (3 mols.) to a boiling solution of alcoholic potash (3 mols.), exhausting the product with ether, and distilling the residue from the ethereal extract under a pressure of 25 mm. The ethyl compound thus obtained (yield 54 per cent. of theory) boiled at 143—147° (25 mm.), and melted at 20—22°.

Orthethoxybenzaldoxime, $OEt\cdot C_6H_4\cdot CH{:}NOH$, is formed when ethylsalicylaldehyde is heated with hydroxylamine hydrochloride and excess of soda. It is readily soluble in alcohol, ether, and benzene, sparingly so in water, slightly volatile in a current of steam, has a characteristic odour, and crystallises from light petroleum in colourless, compact prisms which melt at 57—59°.

The *hydrochloride*, $OEt\cdot C_6H_4\cdot CH{:}NOH,HCl$, separates in the form of small, yellow needles, when the base is dissolved in ether and the solution treated with dry hydrogen chloride. It melts at 123—125°, and is reconverted into orthethoxybenzaldoxime on warming with water.

Orthethoxybenzylamine, $OEt\cdot C_6H_4\cdot CH_2\cdot NH_2$, is obtained on dissolving the aldoxime in a little alcohol, and reducing with 4 per cent. sodium amalgam, keeping the solution always slightly acid with acetic acid. The *platinochloride*, $OEt\cdot C_6H_4\cdot CH_2\cdot NH_2,H_2PtCl_6$, is a crystalline, yellow precipitate, and melts at 182°.

Orthethoxybenzonitrile, $OEt\cdot C_6H_4\cdot CN$, is formed on heating in a reflux apparatus a mixture of orthethoxybenzaldoxime (1 mol.) and acetic anhydride (4 mols.). The product is neutralised with soda, extracted with ether, and the ethereal solution distilled, when the compound separates as a colourless oil which boils at 252—254° (260·7° corr.). On heating with alcoholic potash in sealed tubes, it is converted into a mixture of orthethoxybenzoic acid, $OEt\cdot C_6H_4\cdot COOH$, and orthethoxybenzamide, $OEt\cdot C_6H_4\cdot CONH_2$. The latter crystallises from hot water in flat, silky needles, and melts at 132—133°.

With phenylhydrazine, ethylsalicylaldehyde forms a very unstable compound, which is readily oxidised, even by atmospheric oxygen.

The formation of the above-described compounds confirms Perkin's view (*Annalen*, 1868, 306) that the product of ethylation of salicylaldehyde is really orthethoxybenzaldehyde, and shows that the ethyl is not directly attached to a carbon atom (compare Herzig and Zeisel, Abstr., 1888, 822; 1889, 247 and 966). G. T. M.

Pæonol. By W. N. Nagai (*Ber.*, **24**, 2847—2853).—Pæonol was first obtained by Martin and Yagi (*Arch. Pharm.*, **10**), from the bark of the root of *Pæonia moutan*, a drug frequently used in Japan and China. In order to prepare it, the finely-powdered bark is extracted with ether, the extract shaken with sodium carbonate solution to remove impurities, and then with aqueous soda, which takes up the pæonol; the alkaline solution is acidified with sulphuric acid, again extracted with ether, and the residue obtained on evaporating the latter is recrystallised from alcohol. Pæonol is thus obtained in colourless, lustrous needles, having the composition $C_9H_{10}O_3$, and melting at 50°; it has an aromatic odour and burning taste, is sparingly soluble in cold water, readily in alcohol, ether, and benzene. It gives a reddish-violet coloration with ferric chloride, but dissolves

in sulphuric acid without alteration of colour; it also dissolves readily in caustic alkalis, but not in ammonia or solutions of alkali carbonates, which agrees with the supposition that it is a phenol.

When fused with potash, it yields 1 : 2 : 4-dihydroxyacetophenone (resacetophenone), $C_6H_3Ac(OH)_2$, α-resorcylic acid, $COOH{\cdot}C_6H_3(OH)_2$ [1 : 2 : 4], and resorcinol; the first is probably the primary product, the other compounds being formed from it by the further action of alkali. Hydriodic acid converts it into methyl iodide and resacetophenone, of which it must therefore be the methyl ether. To ascertain which of the hydroxyl groups is methylated, the acetyl derivative was prepared by boiling pæonol with acetic anhydride for 30 hours, extracting any unaltered pæonol with light petroleum (b. p. 55—57°), and recrystallising the residue from alcohol. *Acetylpæonol*, $C_9H_9O_3Ac$, is thus obtained in flat, lustrous needles melting at 46·5°. If instead of acetic anhydride a mixture of this compound with anhydrous sodium acetate is employed, two condensation products are obtained, melting at 130° and 160° respectively; these are being further examined.

By oxidation with alkaline potassium permanganate, acetylpæonol yields paramethoxyacetylsalicylic acid, $COOH{\cdot}C_6H_3(OAc){\cdot}OMe$ [1 : 2 : 4], which, on treatment with strong aqueous potash, is converted into paramethoxysalicylic acid, $COOH{\cdot}C_6H_3(OH){\cdot}OMe$ [1 : 2 : 4], the properties of which were found to agree with previous statements (Abstr., 1881, 270; *Ber.*, **14**, 847), except as regards the melting point, which the author finds to be 156°. The formation of this acid shows conclusively that the methoxyl group occupies the para-position with respect to the acetyl group, and hence pæonol may be termed *paramethoxyorthohydroxyacetophenone*, $OH{\cdot}C_6H_3Ac{\cdot}OMe$ [= 2 : 1 : 4]. H. G. C.

Pæonol Phenylhydrazone and Oxime. By F. Tiemann (*Ber.*, **24**, 2854—2855).—Although pæonol, according to Nagai, does not form a double compound with sodium hydrogen sulphite, it readily combines with phenylhydrazine and hydroxylamine. *Pæonol phenylhydrazone*, $C_9H_{10}O_2{:}N_2HPh$, is prepared by the addition of phenylhydrazine hydrochloride and sodium acetate to an aqueous solution of pæonol, and crystallises from alcohol in pale-yellow needles, melts at 107°, is readily soluble in ether and benzene, sparingly in alcohol and light petroleum, and almost insoluble in water. *Pæonoloxime*, $C_9H_{10}O_2{:}N{\cdot}OH$, separates in needles when its alcoholic solution is poured into water; it is almost insoluble in cold, readily soluble in hot water, and in alcohol, ether, &c.

Pæonol itself may be readily purified by distillation in a current of steam and recrystallisation from hot water. It then melts at 48°, and not at 50°, as stated by Nagai (see preceding abstract).

H. G. C.

Acetovanillone. By F. Tiemann (*Ber.*, **24**, 2855—2862).—In the course of his researches on the members of the protocatechuic series, the author, in conjunction with Nagai (this Journal, 1877, ii,

339), showed that acetylengenol, on oxidation and subsequent hydrolysis, gives a product from which α-homovanillic acid, vanillic acid, and vanillin, may be isolated; in addition to these, a large quantity of a resinous mass is obtained, which, on dry distillation, gives guaiacol as the sole recognisable product. Further investigation of this resin in larger quantity has shown that a crystalline compound may be obtained from it, by neutralising the free acid present with calcium or magnesium carbonate, repeatedly extracting with boiling water, and shaking the extract with ether. The ethereal solution is then treated with sodium hydrogen sulphite to remove vanillin, the ether evaporated, and the oily residue repeatedly washed with water, and distilled under a pressure of 50 mm. The distillate solidifies on cooling, and may be purified by dissolving it in aqueous soda, reprecipitating with carbonic anhydride, extracting again with ether, evaporating the latter, and recrystallising the residue from boiling water, alcohol, or benzene. The new compound then forms long prisms, melts at 115°, boils at 295—300°, and may be readily sublimed. The analysis and molecular weight determinations lead to the formula $C_9H_{10}O_3$, and it is termed *acetovanillone* for the reasons stated below.

Acetovanillone has the properties of a phenol, yields protocatechuic acid when fused with potash, and contains one methoxyl group, as found by Zeisel's method. It therefore contains the residue $:C\cdot C_6H_3(OMe)\cdot OH$. The remaining atoms, C_2H_3O, must be present as an acetyl group, for acetovanillone yields an oxime and phenylhydrazone, and is also formed, although only in small quantity, by distilling a mixture of calcium acetate and vanillate. On boiling with acetic anhydride, it yields an acetyl compound, which may be readily oxidised to acetovanillic acid and vanillic acid, showing that the hydroxyl and methoxyl groups occupy the same positions as in the last-named compound. Hence, acetovanillone has the constitution $C_6H_3Ac(OMe)\cdot OH$ [1 : 2 : 4], and stands in the same relation to vanillin as acetophenone does to benzaldehyde. Acetovanillone gives, with an excess of ferric chloride, exactly the same reaction as vanillin (Abstr., 1886, 238); the liquid assumes first a deep, bluish-violet colour, and on warming gives a precipitate of insoluble dehydrodiacetovanillone.

The presence of acetovanillone among the products of oxidation of acetyleugenol, $CH_2{:}CH\cdot CH_2\cdot C_6H_3(OMe)\cdot OAc$, is not capable of ready explanation. The simplest way of explaining it would be to suppose that it is present ready formed in the eugenol, or that it is obtained by the oxidation of an isomeride of eugenol, of the formula $CH_2{:}CMe\cdot C_6H_3(OMe)\cdot OH$, either present in the liquid or formed during the reaction; no evidence has, however, been found in favour of these views. To explain its formation from acetoeugenol, one might suppose that the latter first takes up the elements of water, forming the compound $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)\cdot OAc$, and then undergoes oxidation in the ω- and β-carbon atoms of the side chain, yielding $COOH\cdot CH_2\cdot CO\cdot C_6H_3(OMe)\cdot OAc$, which loses carbonic anhydride, forming acetovanillone.

The properties of the substances obtained in this research are given in the following abstract. H. G. C.

Derivatives of Acetovanillone. By E. Neitzel (*Ber.*, **24**, 2863—2868).—Acetovanillone yields a series of phenol salts with the metals of the alkalis and alkaline earths, the former having an alkaline reaction, and all readily undergoing decomposition. The *copper* salt is a yellowish-green, amorphous powder.

By the action of an alcoholic solution of methyl iodide on an alkali salt of acetovanillone, the *methyl* ether, or *acetoveratrone*, $C_6H_3Ac(OMe)_2$, is obtained; it forms rhomboïdal crystals, melts at 48—49°, boils at 207° under 15 mm. pressure, is soluble in hot water, alcohol, ether, and benzene, and is converted by potassium permanganate into veratric acid. The corresponding *ethylacetovanillone* forms radial groups of needles, and melts at 78°. *Acetylacetovanillone*, $OMe{\cdot}C_6H_2Ac{\cdot}OAc$, prepared by boiling acetovanillone with acetic anhydride, crystallises from alcohol, on the addition of water, in long needles melting at 58°, and yields vanillic acid on oxidation. *Benzoylacetovanillone*, $OMe{\cdot}C_6H_3Ac{\cdot}OBz$, obtained from an alkaline solution of acetovanillone by the action of benzoic chloride, melts at 106°.

Acetoprotocatechone, $C_6H_3Ac(OH)_2$, is formed in small quantity by the action of hydrochloric acid on acetovanillone at 140—150°, and separates from chloroform solution, on the addition of light petroleum, in crystals which melt at 96—98°. The same compound appears to be formed by the action of zinc chloride on a mixture of catechol and acetic acid, but could not be separated from the excess of catechol.

Acetovanillonephenylhydrazone, $N_2HPh{:}CMe{\cdot}C_6H_3(OMe){\cdot}OH$, forms well-developed crystals, melts at 125°, and is soluble in alcohol and ether; the *oxime*, $OH{\cdot}N{:}CMe{\cdot}C_6H_3(OMe){\cdot}OH$, melts at 95°, is fairly soluble in water, and crystallises best from benzene. *Ethylacetovanillonoxime*, $NOH{:}CMe{\cdot}C_6H_3(OMe){\cdot}OEt$, crystallises from alcohol in lustrous prisms melting at 116—118°. As already mentioned in the preceding abstract, ferric chloride converts acetovanillone into *dehydrodiacetovanillone*, $C_{18}H_{18}O_6$, which is almost insoluble in the usual solvents, and melts above 300°.

When a mixture of calcium acetate and vanillate in molecular proportions is distilled, acetovanillone passes over in small quantity together with acetone, guaiacol, &c. These are removed by distilling in a current of steam, and the residue purified by repeatedly precipitating the benzene solution with light petroleum. H. G. C.

Synthesis of Acetovanillone from Guaiacol and Acetic Acid. By T. Otto (*Ber.*, **24**, 2869—2870).—Acetovanillone may be obtained synthetically by dissolving 60 parts of guaiacol in 120 parts of acetic acid, and gradually adding 30—40 parts of a mixture of zinc and aluminium chlorides in equal proportions; the whole is warmed on the water-bath after the frothing has moderated, and finally heated at 140—150° until hydrogen chloride is no longer evolved. The product is then poured into water, the unaltered guaiacol removed by distillation in a current of steam, the solution filtered from resinous matters, and extracted with ether; the residue from the ethereal solution is treated with soda, the aqueous solution saturated with carbonic anhydride and again extracted with ether, the latter distilled off,

the residue fractionated, and finally recrystallised from boiling water. The acetovanillone thus obtained crystallises in white needles, melts at 115°, and has all the properties ascribed to it in the previous abstracts; the yield of the pure compound is, however, very small.

H. G. C.

Aromatic Hydroxyketones. By P. Crépieux (*Chem. Centr.*, 1891, ii, 377; from *Schweiz. Wochenschr. Pharm.*, **29**, 255—256).—Applying the same method as Nencki used to produce hydroxyketones, the author has obtained from resacetophenone, a substance of the formula $C_6H_2Ac_2(OH)_2$, and from gallacetophenone, a compound,

$$C_6HAc_2(OH)_2{\cdot}OAc.$$

The latter is hydrolysed by potash, one acetyl group being eliminated, and the compound $C_6HAc_2(OH)_3$ formed. By the action of glacial acetic acid and fused sodium acetate on propionylphenol, resacetophenone, gallacetophenone, the acetyl derivatives acetylpropiophenone, monacetylresacetophenone, diacetylgallacetophenone are formed. Where more than one hydroxyl group was present, one remained intact, the others becoming acetylated.

J. W. L.

Constitutents of Paracoto Bark. By G. Ciamician and P. Silber (*Ber.*, **24**, 2977—2990).—The authors find that hydrocotoïn, to which they assigned the formula $OH{\cdot}C_6H_2(OMe)_2{\cdot}COPh$ (*Ber.*, **24**, 299; Abstr., 1891, 578), yields neither an oxime nor a hydrazone; many ketonic compounds are, however, indifferent towards hydroxylamine and phenylhydrazine (compare Hantzsch, Abstr., 1891, 36), and in the case under discussion, this behaviour is perhaps explained by the position of the methoxyl groups in the molecule. The compound is not attacked by aqueous alkalis, but when heated with alcoholic potash under pressure, benzoïc acid and a phenolic compound, apparently a mixture, are formed. When hydrocotoïn (10 grams) is intimately mixed with phosphorus pentachloride (60 grams), and the mixture slowly distilled until all the phosphorus trichloride and oxychloride have passed over, the residue and the distillate being then mixed with water, united, and steam distilled, benzotrichloride first passes over, and then very slowly a solid compound, $C_8H_7Cl_3O_2$; this crystallises from alcohol in colourless needles, melts at 174°, and is insoluble in alkalis; it yields methyl chloride when heated with hydrochloric acid at 140°, and is probably a dimethoxy-derivative. When methylhydrocotoïn (*loc. cit.*) is treated in a similar manner with phosphorus pentachloride, benzotrichloride, together with a *compound*, $C_9H_9Cl_3O_3$, probably a trimethoxy-derivative, is obtained: the latter forms delicate, white needles, and melts at 130—131°; benzoïc acid is found in the aqueous portion of the residue from the steam distillation, whilst by treating the solid portion of the latter with glacial acetic acid and adding water to the solution, a *compound*, $C_{16}H_{14}Cl_2O_4$, separates, which crystallises from alcohol in colourless prisms, melts at 81—82°, and is perhaps dichloromethylhydrocotoïn.

Protocotoïn, $C_{16}H_{14}O_6$, is another constituent of paracoto bark, and occurs as an impurity in crude hydrocotoïn, from which, by reason of its much smaller solubility in alcohol, it may be separated by fractional crystallisation from that liquid. It forms bright-yellow, monoclinic

prisms, $a : b : c = 2{\cdot}9303 : 1 : 2{\cdot}0558$; $\beta = 79° 06'$, melts at 141—142°, is soluble in most solvents, but insoluble in water; it dissolves in alkalis, and is reprecipitated by carbonic anhydride; its solution in dilute alcohol gives a reddish-brown colour with ferric chloride; whilst on treating it with dilute nitric acid, a bluish-green colour is produced, and on heating the solution a reddish-brown precipitate is formed. When its solution in alkalis is reduced with sodium amalgam and acidified, ether extracts a compound crystallising from alcohol in white, amorphous flocks, and melting at 215—220°. A determination by Zeisel's method showed that protocotoïn contains two methoxyl groups. The *acetyl derivative*, $C_{18}H_{16}O_7$, prepared by heating it with an equal weight of anhydrous sodium acetate and four times its weight of acetic anhydride in a reflux apparatus for six hours, forms colourless crystals, melts at 103°, and is insoluble in water and alkalis, but readily soluble in ether, hot alcohol, and chloroform; it dissolves in cold nitric acid to a yellow solution, which, on heating, becomes bluish-green, and finally red; its solution in dilute alcohol gives no coloration with ferric chloride; on boiling with alkalis, protocotoïn is regenerated; it contains one methoxyl group.

Methylprotocotoïn, $C_{14}H_7O_3(OMe)_3$, is obtained by heating together in a sealed tube, protocotoïn (10 grams), a little methyl alcohol, potash (3 grams), and methyl iodide (15 grams), evaporating the alcohol, washing with water, and crystallising from alcohol; it forms colourless prisms, melts at 134—135°, and is insoluble in water and in alkalis. Protocotoïn does not react with hydroxylamine.

The *hydrazone*, $C_{22}H_{20}N_2O_5$, is obtained by heating protocotoïn with an excess of phenylhydrazine, dissolving the melt in glacial acetic acid, pouring it into water, and crystallising the precipitated compound from alcohol; it forms small, colourless prisms, melts at 211°, and is sparingly soluble in alcohol and glacial acetic acid. *Dibromoprotocotoïn*, $C_{16}H_{12}Br_2O_6$, is prepared by treating protocotoïn dissolved in chloroform with an excess of bromine, evaporating the solvent, and crystallising from alcohol; it crystallises in silky scales, melts at 170°, and dissolves in alkalis, in hot dilute nitric acid, and in sulphuric acid with a yellow colour. *Bromacetylprotocotoïn*, $C_{16}H_{15}BrO_7$, is obtained in a similar manner from acetylprotocotoïn; it forms small, delicate, white needles, melts at 175°, and is insoluble in water and cold alkalis, but dissolves in hot alkalis with a yellow colour. Protocatechuic acid is produced when protocotoïn is fused with potash or heated with concentrated hydrochloric acid in a sealed tube at 130°; whilst the compound $C_8H_7Cl_3O_2$, melting at 174°, and identical with that obtained from hydrocotoïn (see above) is produced by treating protocotoïn with phosphorus pentachloride in the manner already described under hydrocotoïn. Methylprotocotoïn, treated in a similar manner, yields the compound melting at 131° identical with that obtained from methylhydrocotoïn. Taking all these facts into consideration, it is probable that protocotoïn has the constitution

$$CH_2\!<^{3\ \ O}_{4\ \ O}\!>C_6H_3{\cdot}CO{\cdot}C_6H_2(OMe)_2{\cdot}OH,$$

which is, however, given under reservation, as the presence of a methylene group has not yet been demonstrated.

When protocotoïn is oxidised in alkaline solution with potassium permanganate, an acid, which is being investigated, together with Jobst and Hesse's paracoumarhydrin (Abstr., 1880, 327), is formed; it contains a carboxyl group, as it yields a *hydrazone*, $C_{15}H_{14}N_2O_2$, melting at 114°. A. R. L.

Vanilloylcarboxylic Acid (Parahydroxymetamethoxybenzoylcarboxylic Acid). By F. Tiemann (*Ber.*, **24**, 2877—2879).—The dimethoxyphenylglyoxylic acid [1 : 3 : 4] recently obtained by Ciamician and Silber by the oxidation of methyleugenol (Abstr., 1890, 966) has already been described by the author and Matsmoto under the name veratroylcarboxylic acid (Abstr., 1878, 503). The corresponding ketonic acid of the vanillin series, or *vanilloylcarboxylic acid*, $COOH{\cdot}CO{\cdot}C_6H_3(OMe){\cdot}OH$ [1 : 3 : 4], has been found in certain vanillin preparations obtained by the oxidation of acetyleugenol, and acetylisoeugenol, and distinguished by their yellow colour. It may be separated from vanillin by shaking with water containing magnesium carbonate in suspension, the vanilloylcarboxylic acid passing into the aqueous solution as a magnesium salt. This is acidified with sulphuric acid, extracted with ether, the latter distilled off, the residue heated at 50—60° in a vacuum and crystallised from benzene. It then forms prisms containing benzene of crystallisation, which is rapidly given off on exposure to the air; after drying at 100°, it melts at 133—134°, and dissolves readily in water, alcohol, ether, and benzene, sparingly in light petroleum. When heated above its melting point, it is resolved into vanillin and carbonic anhydride. H. G. C.

Benzenesulphamides and Mixed Secondary Amines. By O. Hinsberg (*Annalen*, **265**, 178—192).—In a previous paper (Abstr., 1891, 49), it has been stated that phenylsulphonic chloride reacts very readily both with secondary and with primary amines; the compounds obtained from the primary amines are soluble in potash, yielding stable salts, which react readily with fatty and (some) aromatic halogen derivatives, being thereby converted into trisubstituted amines (or disubstituted amides). Various new compounds obtained in this manner are described below.

Benzenesulphonemethylethylamide, $SO_2Ph{\cdot}NMeEt$, is easily obtained by warming a solution of benzenesulphonemethylamide in excess of potash with a little alcohol and excess of ethyl iodide; the yield is quantitative. It is a thick oil, distils under reduced pressure (50 mm.) with only slight decomposition, and is only sparingly soluble in water, acids, and alkalis, but readily in alcohol and ether.

Ethylmethylamine, NHMeEt, is produced when the preceding compound is heated with concentrated hydrochloric acid at 150—160°; it boils at 33—34°, and has properties similar to those of its next homologues. The *hydrochloride*, C_3H_9N,HCl, separates from a mixture of chloroform and ether in colourless, hygroscopic crystals, and is very readily soluble in alcohol; all the other salts are very readily

soluble in water and alcohol, but the *platinochloride* crystallises from the former in moderately large plates.

Benzenesulphonepiperidine, $SO_2Ph{\cdot}C_5NH_{10}$, can be prepared by repeatedly adding small quantities of a mixture of phenylsulphonic chloride and concentrated potash to an aqueous solution of piperidine, and shaking vigorously until the reaction is complete. It crystallises in colourless prisms, melts at 93—94°, and is readily soluble in alcohol and ether, but only sparingly in water; it is decomposed into its components by concentrated hydrochloric acid at 150°.

Benzenesulphonebenzylamide, $SO_2Ph{\cdot}NH{\cdot}CH_2Ph$, prepared from benzylamine and phenylsulphonic chloride, crystallises from dilute alcohol in colourless needles, melts at 88°, and is readily soluble in alcohol and ether, but only sparingly in water. The *methyl* derivative, $SO_2Ph{\cdot}NMe{\cdot}CH_2Ph$, is obtained when the amide is warmed with methyl iodide and alcoholic soda; it is a colourless, crystalline compound, melts at 94°, and is decomposed into benzenesulphonic acid and methylbenzylamine by concentrated hydrochloric acid at 160—180°.

Methylbenzylamine, $CH_2Ph{\cdot}NHMe$, is a colourless liquid, boils at 184°, and has a slight amine-like odour; it is more readily soluble in cold than in hot water. The *sulphate* and the *hydrochloride* are very readily soluble in water. The *platinochloride*, $(C_8H_{11}N)_2,H_2PtCl_6$, crystallises in long, yellowish-red needles, melts at about 193°, and is moderately easily soluble in water. The *nitrosamine* is an oil.

Benzenesulphoneorthotoluidide, $SO_2Ph{\cdot}NH{\cdot}C_6H_4Me$, crystallises from dilute alcohol in colourless needles, melts at 125—126°, and is readily soluble in alcohol and ether, but only sparingly in water: it is insoluble in mineral acids, but it forms stable, readily soluble salts with alkalis.

Benzenesulphoneparaphenetidine, $SO_2Ph{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$, crystallises from alcohol in colourless needles melting at 142°; its *methyl* derivative, $C_{15}H_{17}NSO_3$, crystallises from ether in large plates, and melts at 79°.

Dibenzenesulphonediphenetidine, $C_{28}H_{28}N_2S_2O_6$, can be obtained by gradually adding a concentrated solution of iodine in potassium iodide to a hot, concentrated solution of benzenesulphonephenetidine in sodium carbonate. It crystallises from alcohol in colourless needles, melts at 168°, and is more sparingly soluble in alcohol, ether, and glacial acetic acid than the simple sulphone from which it is obtained; it gives a blue coloration with hot, concentrated sulphuric acid, and forms a crystalline *potassium* derivative of the composition $C_{28}H_{27}N_2S_2O_6K$, which is only sparingly soluble in water, but more readily in alcohol. When heated with concentrated hydrochloric acid at 170°, it yields ethyl chloride, benzenesulphonic acid, and a blue substance which is soluble in alkalis; its constitution is probably expressed by the formula $SO_2Ph{\cdot}NH{\cdot}C_6H_4(OEt){\cdot}N(SO_2Ph){\cdot}C_6H_4{\cdot}OEt$. A *benzyl* derivative of the composition $C_{35}H_{34}N_2S_2O_6$ is formed when the potassium derivative just referred to is treated with benzyl chloride; it crystallises from alcohol in slender, colourless needles, and melts at 158°.

Dibenzenesulphoneparaphenylenediamine, $C_6H_4(NH{\cdot}SO_2Ph)_2$, crystal-

lises in colourless, lustrous plates, melts at 247°, and is readily soluble in alkalis, but only moderately easily in hot alcohol, and almost insoluble in water. The *diethyl* derivative, $C_{22}H_{24}N_2S_2O_4$, crystallises from dilute alcohol, in which it is moderately easily soluble, in colourless needles melting at 197°; on hydrolysis, it yields diethylphenylenediamine, the *diacetyl* derivative of which crystallises from hot water or dilute alcohol in colourless needles, melts at 186—187°, and has the composition $C_{14}H_{20}N_2O_2$.

Dibenzenesulphoneorthotoluylenediamine, $C_6H_3Me(NH\cdot SO_2Ph)_2$, crystallises from alcohol in plates, melts at 178—179°, and is readily soluble in alkalis; its solution in ammonia gives a blue, amorphous precipitate on the addition of copper sulphate. The *diethyl* derivative, $C_{32}H_{36}N_2S_2O_4$, crystallises from alcohol in colourless needles containing $\frac{1}{2}$ mol. C_2H_6O, and melting at about 117° with previous softening; it loses its alcohol at about 120°, and solidifies on cooling to a vitreous mass, which melts at 62—70°.

Diethyltoluylenediamine, $C_6H_3Me(NHEt)_2$, is obtained when the preceding compound is hydrolysed with concentrated hydrochloric acid; it is a colourless oil, boils at 265° (uncorr.), and rapidly darkens on exposure to the air. It gives a reddish-brown coloration with platinic chloride and also with ferric chloride in presence of hydrochloric acid; in its concentrated aqueous solution, potassium ferrocyanide produces a colourless precipitate. Its salts are readily soluble in water, and seem not to crystallise; when the diamine is warmed with phenanthraquinone and acetic acid, it yields a reddish-yellow solution, from which, on evaporation, only amorphous substances are obtained. F. S. K.

Synthesis of Indole from Tartaric Acid and Aniline. By H. Polikier (*Ber.*, **24**, 2954—2959).— Tartranilide (30 grams) is fused in a retort, and, after heating at 260—270° for two hours, slowly distilled over a free flame, until nothing more passes over; the product is then redistilled in a current of steam, when a mixture of aniline and indole passes over, from which the latter can be isolated as picrate, 0·74 gram being obtained; whilst a yellowish residue weighing 4·8 grams remains, which, on crystallisation from alcohol, melts at 220°, and proves to be dianilidosuccinanilide (compare this vol., p. 55). By heating tartranilide (20 grams) with an equal weight of zinc chloride at 270—280° for an hour, dianilidosuccinanilide (1·32 grams) and indole (0·22 gram) may be isolated; whilst, if a mixture of tartaric acid, aniline, and zinc chloride is heated in a sealed tube at 280°, the product extracted with alcohol, and the solution distilled, indole is obtained from the portion of the distillate passing over last, and is purified as described above.

When tartaric acid is added by degrees to boiling orthotoluidine it dissolves after a time, and, on now distilling, the temperature quickly rises to 300°, carbonic anhydride is evolved, and orthotoluidine, methylindole, and a white, crystalline compound melting at 247° pass over; the methylindole is formed in much larger quantity than is indole by the methods described above.

When dianilidosuccinanilide is heated in a sealed tube with a little

water at 200°, a resinous mass, together with aniline and traces of indole is obtained; whilst, if ethyldianilidosuccinic acid (Abstr., 1888, 951) is heated with zinc chloride, a compound melting at about 62°, and giving all the reactions of indole, is produced. It would appear, therefore, that by the action of aniline on tartranilide, dianilidosuccinanilide is initially formed, and this, by the action of water, yields indole, aniline, carbonic anhydride, and carbonic oxide. Further experiments are promised. A. R. L.

Molecular Weight of Nitrosoindole. By C. Zatti and A. Ferratini (*Gazzetta*, **21**, ii, 19—25).—The authors have already noted the comparatively high melting point of the nitrosoindole described by them (Abstr., 1890, 1293), and suggested that its empirical formula might have to be doubled to give the true molecular weight. The molecular weight could not be determined by the cryoscopic method, owing to the very sparing solubility of the substance in the cold, but by observing the elevation of the boiling point of its solution in acetone, numbers were obtained showing that the molecular formula of nitrosoindole is $C_{16}H_{12}N_4O_2$.

Nitrosodimethylindole behaves normally in its solution in acetone, the formula of the molecule being $C_{10}H_{10}N_2O$.

When nitrosoindole is treated with nitric acid, it dissolves, yielding an intensely red solution, and on pouring this into water, a flocculent, blood-red substance separates, which agrees in properties with the so-called nitrosoindole nitrate prepared by Nencki (Abstr., 1875, 1205). W. J. P.

Indazole Derivatives. By C. Paal (*Ber.*, **24**, 3058—3065; compare Abstr., 1891, 723).—Phenylindazole, $C_6H_4<\begin{matrix}N-\\|\\CH\end{matrix}>NPh$ [1 : 2], was dissolved in glacial acetic acid, treated with rather more than the theoretical amount of chromic acid, and boiled in a reflux apparatus until the solution acquired a pure green tint. On diluting the mass with water, *azobenzeneorthocarboxylic acid*, $N_2Ph\cdot C_6H_4\cdot COOH$, separates out, the yield being 70 per cent. of the theoretical. It dissolves easily in ether, alcohol, glacial acetic acid, ethyl acetate, and benzene, very sparingly in hot light petroleum, and not at all in water. It crystallises from alcohol slowly in large, dark-red crystals, or quickly in small needles of the colour of azobenzene. It melts at 95°, and at a higher temperature decomposes with evolution of red fumes, azobenzene being formed. The *alkali salts* and the *barium salt* are easily soluble in water; the *lead salt* forms an orange-coloured, granular, amorphous precipitate which melts in hot water; the *silver salt* forms an unstable, yellowish precipitate, which decomposes when heated, yielding azobenzene, carbonic anhydride, silver, and carbonaceous products. The acid itself is converted into *hydrazobenzeneorthocarboxylic acid*, $NHPh{:}NH\cdot C_6H_4\cdot COOH$, when it is dissolved in alcohol and treated with zinc-dust and a few drops of acetic acid. The new acid separates on pouring the mixture into water. It dissolves easily in mineral acids, ether, alcohol, glacial acetic acid, and ethyl acetate, sparingly in benzene and light petroleum, scarcely at all in

water. It crystallises in yellowish, ill-defined prisms which melt at 165—166°, and, in the air, quickly darken in colour, becoming oxidised to the azo-acid. The white *sodium salt* dissolves readily in water; the *barium salt*, $(C_{13}H_{11}N_2O_2)_2Ba$, forms long, white, hair-like crystals grouped as in wavellite; it oxidises readily in the air.

Benzidinemetacarboxylic acid, $NH_2{\cdot}C_6H_4{\cdot}C_6H_3(NH_2){\cdot}COOH$, is formed to the extent of 60 per cent. of the theoretical yield, when azobenzene-orthocarboxylic acid is reduced by dissolving it in absolute alcohol, excess of tin added, and then hydrochloric acid in successive small proportions, the mixture being heated. On cooling the solution, the *dihydrochloride*, $C_{13}H_{12}N_2O_2,2HCl$, crystallises out in white, lustrous needles which melt at a very high temperature, and do not dissolve in alcohol, but do so in water, undergoing dissociation and forming the *monohydrochloride*, $C_{13}H_{12}N_2O_2,HCl$, which separates in short, dull-white needles; this melts at a very high temperature, and is only sparingly soluble even in hot water. This salt may also be obtained by boiling a hydrochloric acid solution of hydrazobenzeneorthocarboxylic acid. The acid itself is obtained by dissolving either of the hydrochlorides in aqueous ammonia and adding acetic acid. It dissolves sparingly in hot water, hardly at all in absolute alcohol; from dilute alcohol, it crystallises in crusts formed of white needles which melt at 210°, decomposing into carbonic anhydride and benzidine. The *alkali salts* are soluble in water, but insoluble in concentrated alkalis. The *barium salt* forms short, white prisms, almost insoluble in cold water. The *silver salt*, $C_{13}H_{11}N_2O_2Ag$, is a white, amorphous substance, fairly stable in the light, and almost insoluble in hot water.

Parachlorazobenzeneorthocarboxylic acid, $C_6H_4Cl{\cdot}N_2{\cdot}C_6H_4{\cdot}COOH$, is obtained by oxidising parachlorophenylindazole in acetic acid solution with chromic acid, cooling the solution, and diluting it with water. It dissolves readily in hot alcohol, glacial acetic acid, and benzene, scarcely at all in light petroleum. It forms small, orange-coloured, dendritic needles, and melts at 166°. Reduced with zinc-dust and acetic acid, it yields *parachlorhydrazobenzeneorthocarboxylic acid*, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, which is precipitated in white flakes on the addition of water. The yellow *sodium salt* of the azo-acid is soluble in water, but insoluble in concentrated alkalis. The *barium salt* forms lustrous, orange-coloured needles insoluble in water. The *copper salt* forms a bright-green, amorphous, the *silver salt*, a reddish, amorphous, granular, and the *ferric salt*, a bulky, reddish, precipitate.

Parabromazobenzeneorthocarboxylic acid, $C_6H_4Br{\cdot}N_2{\cdot}C_6H_4{\cdot}COOH$, is prepared by oxidising parabromophenylindazole with chromic acid in acetic acid solution. It crystallises from alcohol in small, lustrous, orange-red needles, melts at 176°, and dissolves readily in glacial acetic acid, ethyl acetate, and benzene, but not in light petroleum. It is reduced by zinc-dust and acetic acid to *parabromhydrazobenzene-carboxylic acid*, $C_6H_4Br{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, which forms white, crystalline flakes insoluble in water. The salts of the bromazo-acid resemble those of the chlorazo-acid, except that they are redder, and that the copper and ferric salts are, respectively, bright-green and rusty coloured.

C. F. B.

Synthesis of Indigodisulphonic Acid. By B. Heymann (*Ber.*, **24**, 3066—3070).—A reply to Knietsch (Abstr., 1891, 1231). It is shown that when indigocarmine is obtained from phenylglycocine by dissolving the latter in fuming sulphuric acid (containing 80 per cent. of the anhydride) and removing the excess of anhydride by the addition of concentrated sulphuric acid, the oxygen of the air plays no oxidising part in the reaction, for in an experiment, during which air was carefully excluded, as good a yield was obtained as in other experiments. The author is of opinion that the leuco-compound at first formed has a constitution similar to $HSO_3 \cdot C_6H_3 < \begin{matrix} C(OSO_3H) \\ NH \end{matrix} \!\!\!\

Azines of the Uric Acid Group. By O. Kühling (*Ber.*, **24**, 3029—3033; compare this vol., p. 1341).—*Dimethylnaphthalloxazine*, $C_{10}H_6<\begin{matrix}N{:}C\cdot NMe\cdot CO\\ N{:}C\cdot CO\cdot NMe\end{matrix}$, is prepared by the reaction of tetramethylalloxantin with α-naphthylenediamine hydrochloride in aqueous solution; it crystallises from a mixture of glacial acetic acid and alcohol in small, slender, yellow needles, melts at 285°, and is insoluble in soda or in sodium carbonate solution.

Methylalloxazine, $C_6H_4<\begin{matrix}N{:}C\cdot NMe\cdot CO\\ N{:}C\cdot CO\cdot NH\end{matrix}$, is obtained from orthophenylenediamine hydrochloride and dimethylalloxantin, and crystallises from a mixture of alcohol and glacial acetic acid in small, pale-yellow needles, melting at 250°. The compound is soluble in sodium carbonate solution at the ordinary temperature, and is reprecipitated unchanged by acids.

Methyltolualloxazine, $C_6H_3Me<\begin{matrix}N{:}C\cdot NMe\cdot CO\\ N{:}C\cdot CO\cdot NH\end{matrix}$, is formed from 1 : 3 : 4-orthotoluylenediamine hydrochloride and dimethylalloxantin; it resembles the preceding compound in properties, and blackens when heated above 250°.

Methylnaphthalloxazine, $C_{10}H_6<\begin{matrix}N{:}C\cdot NMe\cdot CO\\ N{:}C\cdot CO\cdot NH\end{matrix}$, is deposited on heating α-naphthylenediamine hydrochloride with dimethylalloxantin in aqueous solution; it is insoluble in water, very sparingly so in alcohol, and crystallises from glacial acetic acid in slender, yellow needles. The azine dissolves in soda or in sodium carbonate solution on gently warming, and is precipitated unchanged by acids; it is unaltered by heating at about 300°. On boiling aqueous solutions of orthodiamine hydrochlorides with parabanic acid, sparingly soluble compounds are obtained, which proved on analysis to be dihydroxyquinoxalines; these compounds are formed by the resolution of the parabanic acid into carbamide and oxalic acid, and the condensation of the latter compound with the orthodiamine. *Naphthadihydroxyquinoxaline*, $C_{10}H_6<\begin{matrix}N{:}C\cdot OH\\ N{:}C\cdot OH\end{matrix}$, is prepared by heating parabanic acid with α-naphthylenediamine hydrochloride for several hours in aqueous solution; it is purified by dissolving in dilute potash and precipitating with hydrochloric acid, and forms slender, colourless needles which melt above 300°. The compound dissolves in glacial acetic acid, and sparingly in alcohol, but is insoluble in water. The *barium salt* is insoluble in water and is decomposed by acids.

The substituted parabanic acids appear to be more stable towards orthodiamines; cholestrophane is unaffected by orthotoluylenediamine hydrochloride, and allantoïn does not react at all with orthodiamines. J. B. T.

A Volatile Oil from Aristolochia reticulata. By J. C. Peacock (*Chem. Centr.*, 1891, ii, 379; from *Amer. J. Pharm.*, June, 1890).—From the rhizomes of this plant, as they are obtained com-

mercially, the author separated 0·61—0·94 per cent. of a golden-yellow oil. It has a camphor-like odour and taste, dries slowly when exposed to the air, does not solidify at −17°, and has a sp. gr. of 0·9745—0·9785 at 15·5°, and 0·9719—0·9758 at 20°. It is miscible with alcohol, ether, chloroform, benzene, and light petroleum; it exhibits no aldehyde reaction, and rotates the polarised ray −4° in 100-mm. tube. By fractional distillation, 10 per cent. passed over at 74—75° under a pressure of 43 mm., 60 per cent. between 122—124°, under a pressure of 43 mm., and 20 per cent. between 147—150° under a pressure of 47·7 mm.; the residue in the retort possessed a blue and green fluorescence, and contained tarry matters.

This first distillate boiled at 157° under a pressure of 769·6 mm.; its sp. gr. was 0·865 at 15·5°; its formula is $C_{10}H_{16}$, with which its vapour density corresponded; it absorbs bromine very readily, and is characterised as a member of Wallach's pinene group.

The second fraction boils at 211° under 763·6 mm. pressure; its formula is $C_{15}H_{25}O_2$, with which the vapour density corresponds. On hydrolysis with potash, a camphor, $C_{10}H_{18}O$, is produced, which is very similar to borneol; it boils at 199·5—200°. An acid is also separated of the probable formula $C_5H_9O_2$; melting point about 65°; it forms a red precipitate with ferric chloride; its odour is unpleasant.

The third fraction, boiling at 239—240°, under 762·1 mm. pressure, is a greenish-yellow oil; sp. gr. 0·9888 at 15·5°; its formula is $C_{18}H_{29}O$, with which the vapour density corresponds; it is a neutral, indifferent substance. J. W. L.

Bergapten, the Stearoptene of Bergamot Oil. By C. Pomeranz (*Monatsh.*, **12**, 379—392).—This substance separates as a crystalline magma when the ethereal oil obtained from the rind of the fruit of *Citrus bergamia* is kept for some time. It may be purified by sublimation or by recrystallisation from alcohol, when it forms hard, white, silky needles, which are tasteless and odourless at ordinary temperatures, but evolve aromatic vapours when heated. It is slightly soluble in cold alcohol and in hot water; dissolves in hot alcohol, acetic acid, chloroform, benzene, and phenol, and melts at 188°, with partial sublimation. Elementary analysis and a determination of its molecular weight by observing the depression of the freezing point of a solution in phenol show that it has the molecular formula $C_{12}H_8O_4$. Aqueous and alcoholic potash, acetic anhydride, phenylhydrazine, and boiling hydrochloric acid are all without action on the compound, which, however, as shown by the action of hydriodic acid and acetic anhydride (compare Herzig, *Monatsh.*, **9**, 544), contains three methoxyl groups.

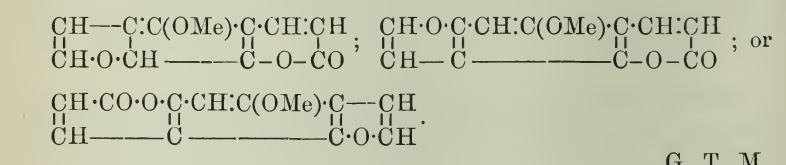
On heating bergapten with potash, methyl alcohol, and methyl iodide in a reflux apparatus for five hours, two new compounds are obtained. One of these has the formula $C_{14}H_{14}O_5$; crystallises from alcohol in microscopic prisms, which are far more soluble in alcohol, chloroform, and ether than is bergapten, and melts at 52°. The other, which the author has named *methylbergaptic acid*, contains CH_2 less than the preceding compound, which is probably its methyl salt

since, on hydrolysis with potash, it furnishes the free acid. It crystallises from dilute alcohol in small, rhombic plates, dissolves readily in alkaline hydroxides and carbonates, and melts at 138°. When, in the above described operation, ethyl iodide is substituted for methyl iodide, *ethylbergaptic acid* is obtained; this crystallises in acute-angled prisms or in twinned or clustered needles, and melts at 142°. From its behaviour with methyl and ethyl iodides, bergapten must be regarded as the anhydride, $C_{11}H_8O_2<\begin{matrix}O\\|\\CO\end{matrix}$, and it, therefore, closely resembles coumarin in constitution.

When fused with potash, bergapten gives rise to phloroglucinol, and on treatment with two molecular proportions of bromine, the anhydride is converted into monobromobergapten dibromide, $C_{12}H_7O_4Br_3$, formed from bergapten, which has two double linkages in the side chains, by the addition of four atoms of bromine, one of which is afterwards eliminated in the form of hydrobromic acid.

On reduction with sodium amalgam, methylbergaptic acid is converted into *methylhydrobergaptic* acid, $C_{13}H_{14}O_5$, which crystallises from dilute alcohol in small, white needles, and melts at 122°. This product is analogous to the hydro-acids obtained on the reduction of methyl- and ethyl-coumaric acids.

The above-described reactions of bergapten point to its having one of the following constitutions:—



G. T. M.

Action of Sodium Alkyloxides on Camphor. Preparation of Alkylcamphors. By A. Haller (*Compt. rend.*, **112**, 1490—1494). —*Action of Sodium Ethoxide on Camphor.*—At 100° there is no reaction. 5 grams of camphor and 30 c.c. of absolute alcohol to which 0·75 gram of sodium has been added are heated in sealed tubes for 24 hours at 200°. A great pressure is observed on opening the tubes, due to the disengagement of large quantities of hydrogen. The product is treated with water, and the separated, coloured, viscous mass dissolved in ether, from which it separates on spontaneous evaporation of the solvent. Repeatedly crystallised from a mixture of ether and light petroleum, it forms white, hexagonal crystals, melting at 208—210°. This substance is a mixture of dextro- and lævo-borneol, the proportions varying with the preparation. The rotatory powers of two preparations were $[\alpha]_D = +12{\cdot}5°$ and $[\alpha]_D = +16°$.

15 grams of camphor yield 8—10 grams of pure borneol. The yield is better than with Berthelot's method; the product is not mixed with camphor, and only contains traces of camphic acid, small quantities of a liquid product insoluble in water and alkalis, and sodium acetate.

Sodium propoxide, isobutoxide, and amyloxide yield borneol, the quantity decreasing with the rise in the molecular weight of the alcohol employed. Secondary liquid products intermediate in composition between alkylcamphors and alkylborneols increase in the same ratio.

Action of Sodium Benzyloxide on Dextrocamphor. Benzylcamphor.—Dry dextrocamphor (1 mol.) is heated with sodium benzyloxide (1 mol.), dissolved in excess of benzyl alcohol, at 220—225° for 24 hours. There is no disengagement of gas. Distillation of the ethereal extract at 220—225° (H = 70 mm.) yields a syrupy, very refractive substance, which, at first, has a slight empyreumatic odour, becoming similar to the odour of benzaldehyde on exposure to the air. Boiling alcoholic potash, glacial acetic acid, or hydrochloric acid does not attack this substance. It crystallises on cooling, after the addition of a crystal of benzylcamphor, in small crystals which, when recrystallised from alcohol, yield fine, large crystals melting at 51—52°, soluble in alcohol, ether, benzene, and toluene, and insoluble in water and the alkalis. The formation of benzylcamphor is accompanied by the production of an equivalent amount of sodium benzoate and the liberation of hydrogen, which, doubtless, acts on a part of the benzylcamphor yielding reduction products which remain in the uncrystallisable oil.

Benzylcamphor may also be obtained by the action of benzyl chloride on sodiumcamphor when heated. The reaction is finished when a portion of the material, diluted with water, does not give an alkaline reaction. When distilled at 110 mm. pressure, a mixture of camphor and oily products passes over below 200°; from 215—220°, benzylborneol passes over; whilst from 220—250°, a fraction distils as a thick oil, crystallising on cooling. The crystals, purified by recrystallisation from alcohol, correspond in properties with the benzylcamphor prepared from sodium benzyloxide.

Benzalcamphor also yields benzylcamphor on reduction with sodium amalgam.

Benzylcamphoroxime, $C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ CH{\cdot}CH_2Ph\end{matrix}$, is obtained by heating for two days benzylcamphor, mixed with the theoretical amount of the double chloride of zinc and hydroxylamine and a little alcohol. The product crystallises from alcohol in long, flat prisms melting at 127—128°, soluble in ether, benzene, and light petroleum, insoluble in alkalis. The oily liquid separated from the oxime solidifies in time; it has not been examined, but is, doubtless, an isomeride.

Lævobenzylcamphor may be prepared from lævocamphor by the methods given above. The crystals melt at 50—52°. Benzylborneols are formed, together with benzylcamphors, when the camphor iodides are treated with benzyl chloride. They are separated from the benzylcamphors with some difficulty, owing to the approximation of the boiling points. They are oily liquids, having the odour of bitter almonds, and distilling at 215—216° under a pressure of 80 mm.

The oily products obtained by treating camphor at a high temperature with sodium propoxide, butoxide, and amyloxide are held to contain the propyl-, butyl-, and amyl-camphors. W. T.

Action of Sodium Benzyloxide on Ethyl Camphocarboxylate. By J. Minguin (*Compt. rend.*, **112**, 1454—1455).—20—30 c.c. of benzyl alcohol to which has been added 0·5 gram of sodium is heated with 10 grams of ethyl camphocarboxylate at 150° for 24 hours. The resulting pasty mass yields an oil on treatment with water. On evaporating the ethereal solution, the residue yields benzyl alcohol and a viscous liquid distilling at 260—290° under 10 mm. pressure. This is *benzyl hydroxycamphocarboxylate*,

$$C_7H_7O\cdot CO\cdot C_8H_{14}\cdot CH_2\cdot COOC_7H_7.$$

The yield is about 30 grams from 40 grams of ethyl camphocarboxylate. Hydrolysis with alcoholic potash in sealed tubes gives benzyl alcohol and hydroxycamphocarboxylic acid. The rotatory power in alcohol is $[\alpha]_D = +35·5°$.

The wash waters, on neutralisation with an acid, yield an oil which distils at 250—275° at a pressure of 10 mm. This acid is very viscous at the ordinary temperature. On hydrolysis, it gives benzyl alcohol and hydroxycamphocarboxylic acid. It may be considered to be benzylhydroxycamphocarboxylic acid, $COOH\cdot C_8H_{14}\cdot CH_2\cdot COOC_7H_7$. Its rotatory power in alcoholic solution is $[\alpha]_D = 52·62°$.

W. T.

New Method for Determining the Constitution of Homologues of Pyrroline. By C. U. Zanetti (*Gazzetta*, **21**, ii, 25—32).—Ciamician and Zanetti (Abstr., 1890, 1155) showed that hydroxylamine reacts with members of the pyrroline series, yielding dioximes, which are oximes either of diketones or of ketoaldehydes, according to the constitution of the pyrroline. By boiling the resulting oxime with 30 per cent. potash, the author finds that the corresponding bibasic or keto-acid is obtained. This reaction furnishes a means of determining the constitution of the pyrroline homologue employed.

Hydroxylamine and pyrroline react to form succindialdoxime; when this is boiled with 30 per cent. caustic potash there is an abundant evolution of ammonia, and succinic acid, amounting to 70 per cent. by weight of the oxime employed, may be extracted from the solution.

2 : 4-Dimethylpyrroline, on treatment with hydroxylamine, yields α-methyllevulindioxime, which, when boiled for $2\frac{1}{2}$ hours with caustic potash, gives the β-acetoisobutyric acid prepared by Bischoff (Abstr., 1881, 412). The *hydrazone* of this acid crystallises from alcohol in splendid, yellowish scales melting at 122°, with evolution of gas, to a yellow liquid; it is soluble in glacial acetic acid, alcohol, ether, benzene, and ethyl acetate, sparingly so in cold dilute alcohol, and insoluble in water or light petroleum. It dissolves in solutions of the alkaline carbonates with effervescence, and is precipitated unaltered by acids. On exposure to air and light, it is converted into a heavy, reddish-brown liquid. *Ethyl β-acetoisobutyrate* is obtained as a liquid of fruity odour on passing dry hydrogen chloride through a strongly cooled solution of the acid in absolute alcohol. Its *hydrazone*, which separates from dilute alcohol in yellowish scales, melts at 105°, and is soluble in alcohol, ether, ethyl acetate, and acetic acid, sparingly so in cold, dilute alcohol, and insoluble in water and alkaline

carbonates. Like the hydrazone of the free acid, it liquefies on exposure to air and light. W. J. P.

Methyldipyridyls. By A. Heuser and C. Stoehr (*J. pr. Chem.* [2], **44**, 404—410).—$\alpha\alpha$-Dimethyldipyridyl (Abstr., 1891, 80) is better isolated by extracting the base, which separates from the aqueous solution of the reaction mass, with ether, drying the ethereal solution over potassium hydroxide, distilling off the ether, re-dissolving in absolute alcohol, and converting the base into hydrochloride by a stream of dry hydrogen chloride.

When $\alpha\alpha$-dimethyldipyridyl is oxidised with permanganate, three acids are obtained, namely, α-methyldipyridyl-α-carboxylic acid, dipyridyl-$\alpha\alpha$-dicarboxylic acid, and lutidinic acid, in the proportion of 10, 2, and 2 grams respectively, from 20 grams of the base. Five grams of the base are introduced into a solution of 12 grams of potassium permanganate in 1200 grams of water, and the solution is kept at 40° for about 14 days. The manganese dioxide is then filtered off, the filtrate evaporated in a stream of carbonic anhydride, and neutralised with nitric acid. By evaporation with alcohol, most of the potassium nitrate is separated, and the acids are then precipitated with silver nitrate; the silver salts are decomposed by hydrogen sulphide, when a yellow precipitate separates as the hot filtrate cools; this contains the mono- and di-carboxylic acids, which can be separated by the greater solubility of the former in hot water; the lutidinic acid is extracted from the filtrate from the yellow precipitate by evaporation with ammonia and extraction with ether.

α-Methyldipyri yl-α-carboxylic acid has been already described (Abstr., 1891, 81). When heated with glacial acetic acid at 180°, it is converted into methyldipyridyl with evolution of carbonic anhydride.

Dipyridyl-$\alpha\alpha$-dicarboxylic acid, $C_{10}H_6N_2(COOH)_2 + H_2O$, crystallises in colourless needles, melts at 247·5°, decomposes at a slightly higher temperature, and dissolves sparingly in water and glacial acetic acid. It is coloured reddish-yellow by ferrous sulphate when in aqueous solution, and violet when crystalline. The *silver* and *barium* salts were obtained, and also an easily soluble *platinochloride*. When this acid is heated with glacial acetic acid in a sealed tube at 180°, it yields $\gamma\gamma$-dipyridyl, which melts at 111—112° (Weidel gives 114°, Abstr., 1883, 483); the *platinochloride* of this base was obtained, and it is noted that potassium ferrocyanide gives a red-brown solution with the base, from which transparent, six-sided tables gradually separate (compare Abstr., 1891, 80).

Lutidinic acid, $C_5H_3N(COOH)_2 + H_2O$ [$(COOH)_2 = \alpha : \gamma$], crystallises in aggregates of colourless needles, melts at 232—233° with rapid evolution of gas, and dissolves easily in hot water.

A. G. B.

Preparation of α- and β- Pyridyllactic Acid from α-Picoline. By A. Einhorn (*Annalen*, **265**, 208—238).—Pyridyl-ω-trichloro-α-hydroxypropane (Abstr., 1887, 845) is best prepared by heating a solution of α-picoline (50 c.c.) and chloral (45 c.c.) in amyl acetate (175 c.c.) for 10 to 12 hours at 140—150°; the product is extracted

from the solution by shaking with dilute hydrochloric acid. The yield of the hydrochloride is at least 125 grams from 100 grams of picoline; this salt crystallises from alcohol in long, prismatic needles, and melts at 201—202°. The free base crystallises from dilute alcohol in hexagonal plates melting at 86—87°. The *hydrobromide*, $C_8H_9NOCl_3,HBr$, forms well-defined crystals, and melts at 207—208°.

Pyridyl-ω-trichloropropylene, $C_5NH_4{\cdot}CH{:}CH{\cdot}CCl_3$, can be obtained by gradually adding phosphorus pentachloride to a boiling mixture of pyridyltrichlorohydroxypropane hydrochloride and chloroform, and decomposing the salt thus produced with sodium carbonate; it crystallises from alcohol in prismatic needles, melts at 97°, and gradually decomposes on keeping.

α-Pyridyllactic acid, $C_5NH_4{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$, is formed when an aqueous solution of pyridyltrichlorohydroxypropane hydrochloride is gradually added to boiling sodium carbonate, and the heating continued until the reaction is at an end; it is isolated by means of its basic copper salt. It crystallises from alcohol in transparent, seemingly monoclinic prisms, melts at 124—125°, and is only sparingly soluble in ethyl acetate, but more readily in chloroform. The basic *copper* salt, $(C_8H_8NO_3)_2Cu,CuO$, crystallises from hot water and ammonia in slender, green needles. The *silver* salt, $C_8H_8NO_3Ag$, crystallises from dilute ammonia in colourless needles. The *hydrochloride*, $C_8H_9NO_3,HCl$, separates from alcohol in crystalline aggregates, and melts at 85—86°. The *hydrobromide*, $C_8H_9NO_3,HBr$, crystallises from glacial acetic acid and alcohol in large, well-defined needles melting at 125—126°. The *platinochloride*, $(C_8H_9NO_3)_2,H_2PtCl_6$, is moderately easily soluble, and melts at 202—204°. The *aurochloride* forms compact, yellow prisms, and melts at 177°. When pyridyllactic acid is heated at 130—140° under reduced pressure, it is converted into pyridylacrylic acid with elimination of 1 mol. H_2O; on oxidation with excess of very dilute potassium permanganate, it yields picolinic acid.

Benzoyl-α-pyridyllactic acid, $C_5NH_4{\cdot}CH_2{\cdot}CH(OBz){\cdot}COOH$, is best prepared by gradually adding benzoic anhydride (4 grams) in small portions at a time to a solution of α-pyridyllactic acid (2 grams) in water (4 grams), heated at a temperature just below 90°; it crystallises from hot water in lustrous needles, and melts at 145° with decomposition. The *platinochloride*, $(C_{15}H_{13}NO_4)_2,H_2PtCl_6$, crystallises from water or dilute alcohol in yellow, transparent, prismatic needles melting at 179° with decomposition. The *barium* salt is a colourless, crystalline compound, readily soluble in water and alcohol; the *silver* salt crystallises in colourless needles. The *methyl* salt, prepared by treating the silver salt with methyl iodide, is an oil, but its platinochloride, $(C_{16}H_{15}NO_4)_2,H_2PtCl_6$, crystallises from hot water and dilute alcohol in yellow needles melting at 193° with decomposition.

Methyl α-pyridyliactate, $C_5NH_4{\cdot}CH_2{\cdot}CH(OH){\cdot}COOMe$, prepared by treating a methyl alcoholic solution of the acid with hydrogen chloride, is a colourless, crystalline compound melting at about 34°; its *aurochloride*, $C_9H_{11}NO_3,HAuCl_4$, separates from water in crystals, and melts at about 119°; its *benzoyl* derivative crystallises in transparent needles, melts at 41°, and is identical with the methyl benzoylpyridyl-α lactate

just described (as an oil), as was proved by converting it into the crystalline platinochloride (m. p. 193—194°).

Pyridylacrylic acid, $C_5NH_4{\cdot}CH{:}CH{\cdot}COOH$ (*loc. cit.*), is best prepared by adding pyridyltrichloropropane hydrochloride (60 grams), in small portions (3 to 4 grams) at a time, to a boiling solution of potassium hydroxide (132 grams) in alcohol (400 grams), air being excluded as much as possible. After boiling for six hours, the filtered solution is evaporated with hydrochloric acid, the residue extracted with alcohol, the extract decolorised with animal charcoal and concentrated; on cooling, pyridylacrylic acid hydrochloride is deposited in crystals, and the mother liquors contain pyridyllactic acid hydrochloride, which can be isolated by means of its copper salt; the yield of the former is 20 grams, and of the copper salt, 5 grams. Pyridylacrylic acid crystallises from boiling water in small, transparent needles, melts at 202—203° with decomposition, and is almost insoluble in cold water, but readily soluble in alcohol. The hydrochloride crystallises from alcohol in colourless needles melting at 220° with decomposition. The *hydrobromide*, $C_8H_7NO_2,HBr$, forms spear-shaped crystals, and melts at 222—223°. The *aurochloride*, $C_8H_7NO_2,HAuCl_4$, crystallises from hot water in small, light-yellow needles, and melts at 194—195°. The *platinochloride*, $(C_8H_7NO_2)_2,H_2PtCl_6$, is moderately easily soluble in water, from which it crystallises in reddish-yellow prisms melting at 209—210°. The barium salt and the salts of the alkalis do not crystallise, but the *calcium* salt, $(C_8H_6NO_2)_2Ca$, separates from dilute alcohol in slender needles; the *silver* salt, $C_8H_6NO_2Ag$, is also crystalline. The *methyl* salt, prepared by treating the acid with hydrogen chloride in methyl alcoholic solution, is a solid, very hygroscopic substance; its *hydrochloride*, $C_9H_9NO_2,HCl$, separates from methyl alcohol in small, colourless crystals melting at 185—186°. The *ethyl* salt crystallises in long, transparent needles. The *methiodide*, $C_8H_7NO_2,MeI$, separates from dilute alcohol in amber-yellow, prismatic needles, and melts at 219—220° with decomposition. The *methobromide*, $C_8H_7NO_2,MeBr$, separates from water in colourless crystals, melts at 242° with decomposition, and is almost insoluble in alcohol, and only sparingly soluble in glacial acetic acid.

Pyridyldibromopropionic acid, $C_5NH_4{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$, prepared by warming pyridylacrylic acid (1 part) with a glacial acetic acid solution of bromine (1·3 parts), separates from water in yellowish crystals melting at 127°, and from glacial acetic acid in grey crystals, which retain some of the solvent, and melt at 146·5°.

β-Pyridylbromopropionic acid hydrobromide,

$$C_5NH_4{\cdot}CHBr{\cdot}CH_2{\cdot}COOH,HBr,$$

is formed when pyridylacrylic acid is heated at 100° with a solution of hydrogen bromide in glacial acetic acid, saturated at 0°; it crystallises in colourless needles or plates, and melts at 163—164°.

Pyridylethylene is produced, together with pyridylacrylic acid and β-pyridyllactic acid, when an aqueous solution of the preceding compound is warmed with a slight excess of sodium carbonate; it is a colourless oil, boils at 159—160° with partial decomposition, and is identical with Ladenburg's vinylpyridine. The *platinochloride*,

$(C_7H_7N)_2,H_2PtCl_6$, separates from water in crystals, and melts at 174° with decomposition. The *aurochloride*, $C_7H_7N,AuCl_3$, crystallises in yellow needles, and melts at 144°.

β-Pyridyllactic acid, $C_5NH_4{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, is isolated from the red solution which remains after distilling the pyridylethylene with steam, by first acidifying with dilute hydrochloric acid to precipitate the pyridylacrylic acid, and then adding an ammoniacal solution of copper sulphate to the filtrate; after a time, the basic *copper* salt, $(C_8H_8NO_3)_2Cu.CuO$, is deposited in blue crystals, and can be purified by recrystallisation from dilute ammonia. The free acid is a crystalline compound melting at 86°. The *hydrochloride*, $C_8H_9NO_3,HCl$, crystallises from alcohol in colourless prisms, and melts at 147°. The *platinochloride*, $(C_8H_9NO_3)_2,H_2PtCl_6$, separates from dilute alcohol in small, yellow crystals melting at 191°. The *methyl* salt, prepared by treating a methyl alcoholic solution of the acid with hydrogen chloride, is a light, yellow oil; its *platinochloride*, $(C_9H_{11}NO_3)_2,H_2PtCl_6$, crystallises from dilute alcohol in lustrous, yellow plates, and melts at 178·5°. The *ethyl* salt is also a pale-yellow oil, but its *hydrochloride* crystallises from alcoholic ether in lustrous plates.

Benzoyl-β-pyridyllactic acid, $C_{15}H_{13}NO_4$, is formed when ethyl β-pyridyllactate is warmed with benzoic chloride on the water-bath; the benzoic acid is separated in the usual way, the product then dissolved in hydrochloric acid, the solution kept for some days, and the crystalline hydrochloride thus obtained decomposed with water: the free acid crystallises from hot water in lustrous prisms, and melts at 135·5°. The *silver* salt is a colourless, crystalline compound. The *methyl* salt, $C_{16}H_{15}NO_4$, prepared from the silver salt, crystallises in transparent prisms, and melts at 79°.

The relationship between some of the compounds described above and certain derivatives of cocaïne is shown with the aid of graphic formulæ. F. S. K.

Synthesis of Quinoline Derivatives by means of Alkyl Acetoacetates. By M. Conrad and L. Limpach (*Ber.*, **24**, 2990—2992).—An extension of the method previously described by the authors (Abstr., 1888, 593) to the synthesis of other quinoline derivatives.

Methyl phenylamidomethylcrotonate is obtained by mixing methyl methylacetoacetate and aniline in equivalent proportions, and allowing the mixture to remain for some days, or by dissolving methyl phenylamidocrotonate in benzene, and treating it first with sodium and then with methyl iodide.

Dimethylhydroxyquinoline, $C_9NH_4Me_2{\cdot}OH$ [$Me_2 : OH = 2' : 3' : 4'$], is obtained by quickly heating methyl phenylamidomethylcrotonate (30 grams) to 240°, withdrawing the source of heat as soon as the temperature reaches 260°, dissolving in dilute hydrochloric acid, treating the solution with animal charcoal, and rendering it faintly alkaline with ammonia or soda, when it separates as a white, crystalline mass; the yield is 10 grams. It crystallises from boiling water in lustrous prisms containing 1 mol. H_2O, sublimes at 300°, melts above 305°, and is only slightly soluble in alcohol; it has not a bitter

taste. The *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, forms long, orange-yellow needles.

Methylethylhydroxyquinoline, $C_9NH_4MeEt{\cdot}OH$, is produced in a similar manner to the dimethyl derivative, by heating methyl phenylamidoethylcrotonate; it melts at 290°, and is only sparingly soluble in boiling water and alcohol. A. R. L.

Action of Hydroxylamine on Ketonic Nitriles. By HANRIOT (*Bull. Soc. Chim.* [3], 5, 773—779).—When ethyl α-cyanethyl ketone, $COEt{\cdot}CHMe{\cdot}CN$ (Abstr., 1889, 841) (100 grams) is dissolved in concentrated potash (200 c.c.), a *potassium* compound is formed, which may be crystallised in brilliant plates; but if the solution is heated on the water-bath for half an hour with a solution of hydroxylamine hydrochloride (100 grams) in the minimum quantity of water, *amidomethylethylisoxazole*, $\begin{matrix}CMe{:}C(NH_2)\\ CEt{=\!=\!=}N\end{matrix}\!\!>O$, separates as an oily liquid, which, on purification, becomes crystalline. It forms highly refractive prisms, melts at 44°, and boils at 180° under a pressure of 20 mm.; at a higher temperature, it changes into an isomeric substance melting at 280°. It is soluble in the usual menstrua, with the exception of petroleum, and is not affected by alkalis. The *hydrochloride*, $C_6H_{10}N_2O,HCl$, crystallises in long needles, and is soluble in water and alcohol, but insoluble in ether. The *acetyl* derivative, $C_9H_9N_2OAc$, crystallises in colourless plates, melts at 161°, and is soluble in alcohol and acetone, sparingly soluble in water, and insoluble in ether.

When an ethereal solution of the isoxazole is saturated with bromine, a yellow, viscous mass is obtained, which is decomposed by water into ammonium chloride and *methylethylbromazolone*,

$$\begin{matrix}CMeBr{\cdot}CO\\ CEt{=\!=}N\end{matrix}\!\!>O,$$

a crystalline substance which melts at 41°, and dissolves in the usual menstrua. If, however, the bromination is effected in chloroform solution, a substance melting at 92° is obtained.

When the isoxazole is oxidised with nitrous acid (sodium nitrite and hydrochloric acid), yellow crystals of the corresponding azoxy-compound are obtained. *Azoxymethylethylisoxazole*,

$$\begin{matrix}CEt{\cdot}CMe & O & CMe{\cdot}CEt\\ \|\ \ \| & /\!\backslash & \|\ \ \|\\ N{\cdot}O{\cdot}C{-\!-}N & -N & -\!-C{\cdot}O{\cdot}N\end{matrix},$$

melts at 65—66°, and explodes at a somewhat higher temperature. It is soluble in alcohol, ether, and alkalis; the alkaline solution is red, and is decolorised by acids, the compound being reprecipitated. It does not unite with bromine.

When hydrogen sulphide is passed through an ammoniacal alcoholic solution of the azoxy-compound, the colour disappears, and on evaporation crystals of *hydrazomethylethylisoxyazole*,

$$\begin{matrix}CEt{\cdot}CMe & & CMe{\cdot}CEt\\ \|\ \ \| & & \|\ \ \|\\ N{\cdot}O{\cdot}C{-\!-}NH & -NH & -\!-C{\cdot}O{\cdot}N\end{matrix},$$

are deposited. When pure, it forms felted needles, melts at 150°, and dissolves in the usual menstrua. It is easily oxidised to the azoxy-compound, and forms an oily compound with bromine.

When ethyl α-cyanisopropyl ketone, $COEt\cdot CMe_2\cdot CN$ (*loc. cit.*), is treated with hydroxylamine hydrochloride, the ring condensation can no longer take place, as the hydrogen previously available for that purpose is replaced by methyl. Consequently, *ethyl α-cyan-isopropyl ketoxime*, $OH\cdot N:CEt\cdot CMe_2\cdot CN$, is obtained, instead of an isoxazole. It crystallises in plates, melts at 61—62°, and is soluble in the usual menstrua with the exception of petroleum. It differs from the isoxazole in that it forms a crystalline potassium derivative when treated with potash, that it does not unite with bromine, and that it is not oxidised with nitrous acid. Jn. W.

Methylphenyldihydroquinazoline and its Derivatives. By C. Paal and F. Krecke (*Ber.*, **24**, 3049—3058; compare Abstr., 1890, 1443).—After orthonitrobenzylacetanilide,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NPhAc\ (1:2),$$

has been reduced with tin and hydrochloric acid, and the stannochloride of methylphenyldihydroquinazoline, $C_6H_4<\begin{matrix}N= CMe\\ CH_2\cdot NPh\end{matrix}$, has been removed by crystallisation, there remains in the mother liquor a varying quantity, never exceeding one-third of the theoretical, of *orthamidobenzylacetanilide*, $NH_2\cdot C_6H_4\cdot NPhAc$. This substance is not formed when the reduction is carried out with zinc-dust and acetic acid. It can be obtained from the mother liquor by removing the tin with sulphuretted hydrogen, and extracting the filtered solution with ether, after previously making it alkaline. It crystallises from alcohol or water in lustrous, white prisms melting at 126—127°, and dissolving easily in alcohol, benzene, carbon bisulphide, ethyl acetate, and glacial acetic acid, moderately in ether, and sparingly in light petroleum and hot water. When oxidised with alkaline permanganate at 100°, it yields, besides a small quantity of azobenzene, a substance of undetermined constitution which crystallises from water in broad, yellowish needles melting at 178°, and from ethyl acetate in crossed crystals; this dissolves sparingly in benzene, easily in alcohol, ethyl acetate, glacial acetic acid, concentrated hydrochloric acid, alkalis, and alkaline carbonates.

Orthamidobenzylacetanilide hydrochloride, $C_{15}H_{16}N_2O,HCl$, is best obtained by adding a little concentrated sulphuric acid and ether to an alcoholic solution of the base. It crystallises in white needles, melts at 170°, and is readily soluble in water and alcohol. The *stannochloride*, $C_{15}H_{16}N_2O,HSnCl_3$, does not crystallise readily; it melts between 110—115°, and dissolves easily in water and alcohol. The *acid sulphate*, $C_{15}H_{16}N_2O,H_2SO_4$, crystallises in stellate groups of colourless needles, which become green on the surface when kept, melts at 163°, and dissolves readily in water. The *oxalate* and the *picrate* are both easily soluble in water and alcohol.

When the base is boiled for a short time with excess of acetic anhydride, and the product treated with a dilute solution of sodium

carbonate, *orthacetamidobenzylacetanilide*, $NHAc\cdot C_6H_4NPhAc$, separates. It crystallises from alcohol in four-sided plates, melts at 121°, and dissolves readily in most organic solvents and in dilute mineral acids, but very sparingly in water.

Methylphenyldihydroquinazoline, previously obtained by reducing orthonitrobenzylacetanilide with tin and hydrochloric acid, is better obtained by using zinc-dust and acetic acid, the solution being kept cool. The solution is then filtered from excess of zinc, and treated with excess of soda; the base is extracted with ether, and converted into the sparingly soluble hydrochloride, which is purified by crystallisation from water. It may also be obtained by distilling orthamidobenzylacetanilide, which loses water and gives almost a quantitative yield of methylphenyldihydroquinazoline. The *acid sulphate* $C_{15}H_{14}N_2,H_2SO_4 + H_2O$, obtained by adding sulphuric acid in slight excess and then some ether to an alcoholic solution of the base, crystallises from water in colourless, interwoven needles. It melts at 78°; when anhydrous, at 201°. When methylphenyldihydroquinazoline is oxidised with alkaline permanganate, the filtered solution contains *phenylketodihydroquinazolinecarboxylic acid*,

$$C_6H_4<\begin{matrix}N:C\cdot COOH\\ |\\ CO\cdot NPh\end{matrix}.$$

This can be separated as a crystalline precipitate by adding hydrochloric acid to the solution; when fresh, it is soluble in hydrochloric acid, alkalis, and alkaline carbonates, but it readily loses carbonic anhydride, yielding *phenylketodihydroquinazoline*, $C_6H_4<\begin{matrix}N:CH\\ |\\ CO\cdot NPh\end{matrix}$. The manganese precipitate contains *methylphenylketodihydroquinazoline*, $C_6H_4<\begin{matrix}N:CMe\\ |\\ CO\cdot NPh\end{matrix}$, which may be extracted with alcohol; it crystallises from that solvent in long, yellowish prisms, melts at 143°, and dissolves readily in ether, alcohol, benzene, and light petroleum, very sparingly in hot water. The *hydrochloride* forms bunches of white needles, melts at a very high temperature, and dissociates in water.

Methylphenyltetrahydroquinazoline, $C_6H_4<\begin{matrix}NH\cdot CHMe\\ |\\ CH_2\cdot NPh\end{matrix}$, was obtained by reducing a hot concentrated alcoholic solution of the dihydrocompound with sodium in large excess, and then diluting the mixture with water. It crystallises from dilute alcohol in broad needles, melts at 94—95°, and dissolves easily in most organic solvents and in mineral acids, but not in water. The *hydrochloride* and *oxalate* were prepared. When heated with acetic anhydride, it yields *acetylmethylphenyltetrahydroquinazoline*, $C_6H_4<\begin{matrix}NAc\cdot CHMe\\ |\\ CH_2\cdot NPh\end{matrix}$, which crystallises from dilute alcohol in colourless, rhomboidal plates, melts at 120·5°, and dissolves readily in the usual organic solvents. C. F. B.

Action of Hydriodic Acid on Quinine. Isoquinine. By E. Lippmann and F. Fleissner (*Monatsh.*, **12**, 327—337; compare Zorn,

Annalen, **8**, 201; Skraup, *J. pr. Chem.* [2], **8**; and Comstock and Koenigs, Abstr., 1887, 1122, and 1888, 71).—*Hydriodoquinine hydriodide*, $HIC_{20}H_{24}N_2O_2,2HI$, is obtained as a heavy, yellow, crystalline powder on warming quinine with hydriodic acid of sp. gr. 1·7—1·8. It is sparingly soluble in cold water; dissolves in hot water with partial decomposition; crystallises from hot alcohol in bright-yellow prisms, melts at 215—230° with decomposition, and, on treatment with dilute ammonia, gives the compound *hydriodoquinine*,

$$C_{20}H_{24}N_2O_2,HI.$$

This substance crystallises in slender needles, softens at 95°, and commences to melt at a higher temperature; gives silver iodide on heating with silver nitrate solution; is insoluble in water, dissolves in alcohol and in ether, and forms soluble salts with acids. *Hydriodoquinine platinochloride*, $HI,C_{20}H_{24}N_2O_2,H_2PtCl_6 + 2H_2O$, is obtained as a light-brown, crystalline precipitate on adding platinum chloride to a cold solution of hydriodoquinine hydriodide in hydrochloric acid.

Hydriodo-apoquinine is prepared by heating hydriodoquinine hydriodide with a solution of hydriodic acid, saturated at 0° for several hours under pressure, at 100°. Methyl iodide is evolved, and, on cooling, the new compound, $HIC_{19}H_{22}N_2O_2,2HI$, separates as a yellow, crystalline mass, which, after recrystallisation from alcohol, commences to darken in colour at 120°, and melts with decomposition at 237°. On the addition of ammonia, 2 mols. of hydriodic acid are removed with formation of hydriodo-apoquinine, of which the platinochloride, $C_{19}H_{22}N_2O_2,HI,H_2PtCl_6 + H_2O$, is a heavy, brown, crystalline powder.

Iso-apoquinine, $C_{19}H_{22}N_2O_2$, is formed on warming hydriodo-apoquinine in alcoholic solution with potash. It melts at 176° (Hesse states that the compound decomposes at 160°), and dissolves readily in dilute potash; the *platinochloride*, $C_{19}H_{22}N_2O_2,H_2PtCl_6 + H_2O$, is a crystalline powder, only sparingly soluble in water.

Isoquinine.—This base is obtained when hydriodoquinine is boiled with alcoholic potash. After repeated crystallisations from ether and dilute alcohol, it melts at 186° (uncorr.). Hesse and Lenz have given the melting point as 174·4—175° and 170·4—174·4° respectively. The base is levorotatory, $[\alpha]_D = -186·75°$ being the rotation of an alcoholic solution containing 0·9644 gram in 100 c.c., and $[\alpha]_D = -180·8°$ for a solution containing 3·9936 grams in 100 c.c. Isoquinine crystallises in small needles containing 2 mols. H_2O; the *sulphate*, $[C_{20}H_{24}N_2O_2]_2,H_2SO_4 + 10H_2O$, forms characteristic groups of slender needles readily soluble in water, giving a ready means of distinguishing between the base and quinine. The *normal hydrochloride*, $C_{20}H_{24}N_2O_2,HCl + 2H_2O$, crystallises in needles, and is readily soluble in water; the *acid hydrochloride*, $C_{20}H_{24}N_2O_2,2HCl$, is not so easily soluble; the platinochloride may be obtained as a crystalline, yellow precipitate; and the compound with silver nitrate, $C_{20}H_{24}N_2O_2,AgNO_3$, is precipitated as a gelatinous mass on adding an alcoholic solution of the base to a solution of silver nitrate. G. T. M.

Compounds of the Cinchona Alkaloïds with Hydriodic Acid. By Z. H. Skraup (*Monatsh*, **12**, 431—434).—Quinine, quinidine, cinchonidine, and cinchonine are all dissolved slowly by cold, and more quickly by warm, hydriodic acid, with the formation of yellow or orange-red coloured compounds, which contain 1 mol. of the base to 3 mols. of the acid; the quinine and quinidine solutions, if kept, further exchange methyl for hydrogen, giving compounds of the formula $C_{19}H_{22}N_2O_2(HI)_3$, which are readily soluble in caustic potash. All these substances crystallise well; they are almost insoluble in water, slightly soluble in absolute alcohol, and dissolve to a moderate extent in dilute alcohol, from which, with care, they may be recrystallised (compare Lippmann and Fleissner, preceding abstract). The compounds from isomeric alkaloïds differ in appearance, solubility, and melting point, and are analogous in composition to the corresponding compounds with hydrochloric and hydrobromic acids (compare Comstock and Koenigs, Abstr., 1887, 1122; and Zorn, *Annalen*, **8**, 20).

When the compounds $C_{20}H_{24}N_2O_2,3HI$ and $C_{19}H_{22}N_2O,3HI$ which are formed from quinine and cinchonidine respectively, are gently warmed with caustic alkalis, they lose 2 mols. of hydrogen iodide, and furnish the compounds $C_{20}H_{25}N_2O_2I$ and $C_{19}H_{23}N_2OI$ respectively. These are analogous in composition to the compounds with hydrochloric acid, which are obtained in a similar way (Comstock and Koenigs, *loc. cit.*). The compounds $C_{20}H_{24}N_2O_2,3HI$ and $C_{19}H_{22}N_2O,3HI$, formed from quinidine and cinchonine respectively, lose only 1 mol. of hydrogen iodide when treated with excess of alkali, the bases $C_{20}H_{26}N_2O_2I_2$ and $C_{19}H_{24}N_2OI_2$, respectively, being produced. The mono- and di-iodine compounds are almost colourless, and must not be regarded as periodids, the hydrogen iodide evidently being held within the molecule. The compounds of the formula $C_{19}H_{22}N_2O_2,3HI$, obtained from quinine and quinidine, and which are soluble in potash, behave in a precisely similar way when treated with alkalis, the compound from the former base losing 2 mols. of hydriodic acid, whilst that from the latter loses only 1 mol. This different behaviour of the products of the action of hydriodic acid with potash forms a convenient means of distinguishing between the isomeric cinchona alkaloïds; and it is also remarkable that those alkaloïds which are decomposed in the same way have a similar effect on circularly polarised light.

Attempts to displace the iodine of the mono- and di-iodine compounds with alkyl groups or other radicles by heating with sodium ethoxide, potash, silver nitrate, &c., invariably led to the elimination of hydrogen iodide. The base $C_{19}H_{24}N_2OI_2$, obtained from cinchonine, however, gave, with sodium ethoxide, in addition to cinchonine, a small quantity of a base which was readily soluble in ether, refused to crystallise, and was probably isocinchonine. The quinidine compound $C_{20}H_{26}N_2O_2I_2$, on similar treatment, did not give the original base, but an isomeride, which is only slightly soluble, and gives salts which crystallise badly. The isomeric quinine compound behaves in an analogous way, but also gives some quinine; whilst the quinine

compound that is soluble in potash does not give rise to cupreïne, but forms an isomeride.

The compounds with hydriodic acid are easily reduced with zinc-dust, and the products appear to be different from those obtained by the reduction of the cinchona alkaloïds. They are semi-liquid, volatile in steam, and very rich in hydrogen.

Quinoline, paramethoxyquinoline, chitenine, and cinchotenine do not combine with hydriodic acid. The author therefore supposes that it is the $C_{10}H_{15}NO$ portion of the quinine molecule that attaches the hydriodic acid, but cannot explain the absorption of 2 mols. of hydrogen iodide, as, even if the oxygen were originally held to a carbon atom by a double bond, only one of the two molecules is accounted for. To explain the addition by assuming a molecular rearrangement of the quinoline nucleus is unsatisfactory, as the hydriodic acid is taken up at ordinary temperatures.

Full particulars of the compounds of the cinchona alkaloïds with hydriodic acid will be given in a future paper. G. T. M.

A new Alkaloïd from Chrysanthemum Flowers. By F. Marino Zuco (*Gazzetta*, **21**, 516—554).—The author has previously extracted from chrysanthemum flowers a new cholesterol (Abstr., 1890, 757), a glucoside, and an alkaloïd (*Rend. Acad. Lincei*, **6**, ii, 572; **7**, i, 121). The latter is prepared in quantity by boiling about 10 kilos. of the flowers in distilled water (3 parts) for 2 or 3 hours, filtering through cloth, pressing the residue, and treating it again in the same manner. The extracts are evaporated down to 30 litres, treated with neutral lead acetate and basic acetate of lead, neutralised with soda, filtered, and the excess of lead removed by passing sulphuretted hydrogen. After filtration, the liquid is concentrated to about 2 litres, boiled for some time with dilute sulphuric acid, filtered, and again boiled until no more resinous matters are formed. The liquid is then decolorised with animal black and an excess of the double iodide of potassium and bismuth added, when a heavy, bright-red, crystalline powder containing the whole of the alkaloïd is deposited.

The pure alkaloïd *chrysanthemine*, $C_{14}H_{28}N_2O_3$, is a colourless syrup which, when kept in a vacuum, partially crystallises in tufts of silky needles, and may be heated without decomposition to 100°, but not beyond that temperature. It dissolves in water forming alkaline solutions which absorb carbonic anhydride from the air; it is also soluble in ethyl and methyl alcohols, but not in ether, chloroform, or benzene. Salts of chrysanthemine yield, with the double iodide of potassium and bismuth, orange-red, flocculent precipitates which become crystalline and bright-red on agitation; with the double iodide of mercury and potassium, a yellowish-white precipitate; with the iodide of platinum and sodium, a brown precipitate; with auric trichloride, a yellow, crystalline precipitate which dissolves on heating and is redeposited on cooling; no precipitate is formed with platinic chloride, picric acid, tannin, or mercuric chloride. The base is optically inactive and physiologically innocuous. Its salts are for the most part soluble in water and even deliquescent; the aurochloride and the double iodide of bismuth and chrysanthemine are insoluble. It is a

biacid base, but in dilute solutions it behaves towards acids as if it were monacid. Both the *hydrochlorides* crystallise in small, colourless, deliquescent needles, very readily soluble in water and alcohol, but only moderately in hot water. The *aurochloride*,

$$C_{14}H_{30}N_2O_3Au_2Cl_8,$$

crystallises in minute, golden-yellow prisms very readily soluble in hot water and in absolute alcohol; when pure, it is not much affected by light. The *platinochloride*, $C_{14}H_{28}N_2O_3,H_2PtCl_6$, crystallises in orange-coloured prisms, and is extremely soluble in water.

On heating chrysanthemine with an excess of methyl iodide for two days at 100°, two methyl groups are taken up, and it is partly converted into a new base in which both nitrogen atoms are combined with hydrogen. The two bases can be separated by taking advantage of the great difference in the solubility of their platinochlorides in water. The *platinochloride* of the new base, $C_{16}H_{32}N_2O_3,H_2PtCl_6$, crystallises in small, orange-coloured needles, dissolves very sparingly in water, but moderately in hot water slightly acidified with hydrochloric acid; it is insoluble in absolute alcohol. The *hydrochloride* is a deliquescent compound which crystallises in a vacuum in tufts of small needles. It is freely soluble in water and in hot absolute alcohol. The free base is a syrupy liquid which becomes partially crystalline after being kept for a long time in a vacuum.

Oxychrysanthemine, $C_{14}H_{26}N_2O_4$, prepared by oxidising chrysanthemine with sodium hypobromite, yields a double iodide with bismuth, crystallising in orange-coloured needles readily soluble in hot water. The alkaloïd is a syrupy liquid which, if kept in a vacuum, is slowly converted into a very deliquescent, crystalline mass. It has an acid reaction, but combines with both acids and alkalis. It forms two hydrochlorides: the *dihydrochloride* is a deliquescent, crystalline mass very soluble in absolute alcohol; the *monohydrochloride* is a colourless, crystalline mass composed of very slender, brilliant needles very soluble in water, but only sparingly in absolute alcohol. The *aurochloride*, $C_{14}H_{28}N_2O_4Au_2Cl_8$, crystallises in brilliant, golden-yellow, hexagonal laminæ freely soluble in hot water. Chrysanthemine strongly resists the action of oxidising agents; on heating a sulphuric acid solution of the base with potassium dichromate and sulphuric acid, it is almost quantitatively converted into oxychrysanthemine; a solution of potassium permanganate, on the other hand, only partially converts it into oxychrysanthemine, carbonic anhydride, ammonia, and traces of trimethylamine being evolved, whilst a portion of the base is completely broken up. Oxychrysanthemine is completely disintegrated by a hot solution of potassium permanganate. Dilute solutions of alkalis have no action on chrysanthemine even after prolonged boiling: very concentrated solutions decompose it into trimethylamine, γ-hydroxybutyric acid, and hexahydropiperidinecarboxylic acid with evolution of hydrogen according to the equation $C_{11}H_{28}N_2O_3 + 4KOH + H_2O = C_6H_{10}NO_2K + C_4H_7O_3K + NMe_3 + K_2CO_3 + 4H_2$. The hexahydropiperidinecarboxylic acid obtained in this way yields a very stable *aurochloride*, crystallising in golden-yellow scales very soluble in hot water, but only very sparingly in cold. It

melts at 150—151° without decomposition. The *hydrochloride* crystallises in plates, and melts at 184—185°. The acid corresponds, therefore, neither with Ost's pipecolinic acid (Abstr., 1883, 791) nor with Ladenburg's nipecotinic acid (Abstr., 1891, 735) but is probably a γ-piperidinecarboxylic acid (hexahydroisonicotinic acid). If chrysanthemine is treated with a moderately concentrated solution of potash, the decomposition takes place more slowly and a small quantity of a product intermediate between chrysanthemine and hexahydropyridinecarboxylic acid is obtained. This compound yields an *aurochloride*, $C_{11}H_{21}O_4NAuCl_3$, crystallising in tufts of reddish-yellow needles. Oxychrysanthemine is decomposed by very concentrated solutions of potash into hexahydropyridinecarboxylic and succinic acids, carbonic anhydride, trimethylamine, and hydrogen. Fuming hydrochloric acid has no action on chrysanthemine even after prolonged heating; concentrated sulphuric acid merely resinifies a very small proportion on boiling. A glacial acetic acid solution of chrysanthemine (1 mol.) dissolves iodine (10 atoms), and on distilling off the solvent in a vacuum, a brown oil is left which does not lose iodine on heating at 150°. Chrysanthemine may be boiled with water for days without change; if, however, a solution of the base in an equal weight of water is fractionally distilled, water alone passes over until the temperature exceeds 150°; trimethylamine then begins to come off, and continues to do so until the temperature reaches 200°, when an oily product accompanies it. If the apparatus is now exhausted, the residue distils over between 200° and 230°, the distillate consisting of a mixture of aqueous solutions of hexahydropyridinecarboxylic acid, amyl glycol, dihydroxyamylpiperidine, trimethylamine, and traces of pyridine bases. The amyl glycol is separated from the mixture in the form of *benzoate*, $C_5H_{10}(OBz)_2$, a colourless, crystalline powder melting at 40°; the hexahydropyridinecarboxylic acid is then removed as aurochloride, and the residue contains *dihydroxyamylpiperidine aurochloride*, $C_{10}H_{21}O_2NAuCl_3$, a yellow, crystalline salt which readily loses a molecule of hydrogen chloride and decomposes at 100°.

From a consideration of all the above reactions, the author arrives at the conclusion that the structure of chrysanthemine is best represented by the formula $\begin{matrix} NMe_3\cdot CH_2\cdot CMe\cdot CH_2\cdot CH_2\cdot OH \\ | \qquad\qquad\quad | \\ O-CO-C_5NH_9 \end{matrix}$.

S. B. A. A.

A new Albumin from Protoplasm. By W. Demme (*Chem. Centr.*, 1891, ii, 257; from *Centr. med. Wiss.*, 1891, 483).—*Cytoglobin*, obtained from the lymphatics, liver, spleen, &c., by pressing, extracting the deposit with alcohol, dissolving the residue in water, and reprecipitating with absolute alcohol, is readily soluble in water, is reprecipitated without coagulation from this solution by absolute alcohol, and may be again dissolved in water. It decomposes hydrogen peroxide. Addition of a mineral acid to the aqueous solution converts it into an albumin, *præglobulin*, which is insoluble in water, and into a substance soluble in water; the same change being effected by heating to boiling. Cytoglobin and præglobulin are but

little soluble in the gastric juice, and still less so in the pancreatic juice. Cytoglobin contains: carbon, 52·4; hydrogen, 6·9; nitrogen, 16·7; sulphur, 3·5; and phosphorus, 4·5 per cent.; præglobulin: carbon, 51·4; hydrogen, 7·6; nitrogen, 23·9; sulphur, 3·4; phosphorus, 3·7 per cent. J. W. L.

Physiological Chemistry.

Influence of Wine on Peptic Digestion. By L. Hugounenq (*Bull. Soc. Chim.* [3], **5**, 849—855).—Fibrin was digested with dilute hydrochloric acid in the presence of various colouring matters and wines. It was found that peptic digestion is considerably hindered by colouring matters, whether occurring naturally in the wine, or added fraudulently, and in the latter case, whether artificial, such as magenta, azoflavine, and methylene blue, or natural, such as the colouring matters of elder and mallow. Plastered wine was found to exercise a less injurious influence than wine containing the full amount of tartrates. Jn. W.

Coagulation of the Blood. By C. A. Pekelharing (*Virchow's Festschrift*, 1891, Bd. 1).—Recently, a number of observations on the importance of calcium salts in the process of blood coagulation have been published.

Brücke first showed that the ash of fibrin always contains calcium. In 1875, Hammarsten found that calcium chloride can take the place of serum globulin in fibrin formation. In 1887, Green (Abstr., 1888, 306) found that in magnesium sulphate plasma, and also in other forms of plasma, coagulation is hastened if small quantities of calcium sulphate is added in addition to fibrin ferment. Later, Ringer and Sainsbury (Abstr., 1890, 1176) found that this result can be brought about by other calcium salts, such as the chloride, and also, but not so readily, by means of soluble strontium and barium salts. Freund (*Med. Jahrb.*, 1888, 259) who also noted the hastening of coagulation by calcium salts, considered that the blood corpuscles, as soon as the blood is shed, yield alkaline phosphates to the plasma; meeting with the calcium salts there, tricalcium phosphate is precipitated, and herein lies the cause of fibrin formation. Latschenberger (*Med. Jahrb.*, 1888, 479), and von Strauch (*Dissert. Dorpat*, 1889) showed certain fallacies in this hypothesis; thus the addition of alkaline phosphates and calcium salts resulting in the precipitation of tricalcium phosphate does not always lead to the formation of fibrin in fibrinogenous liquids; also the first portions of fibrin formed were found to contain calcium, but no phosphoric acid, and further, in the present research, it is shown that injection of disodium phosphate into the circulation of a living animal is not followed by thrombosis.

Arthus and Pagès (*Arch. de Physiol.*, 1890, No. 4) found that blood coagulation may be entirely prevented if, immediately on being shed, the blood is mixed with small quantities of substances, like oxalates

or fluorides, which precipitate calcium salts as very insoluble compounds. On adding to the plasma obtained from this blood a slight excess of calcium chloride, coagulation immediately ensues. Fibrin ferment is, however, essential for the process; and the action of this agent is considered to be the bringing together of fibrinogen and the calcium compound, and thus the formation of fibrin. In this, they draw a close analogy between fibrin formation and the formation of caseïn in milk under the influence of the rennet ferment. Green attempted to answer the question, Does the fibrin ferment exist as zymogen in the plasma, and is such zymogen converted into the ferment by the action of the calcium salt? He was unable to find a positive answer; and therefore considered that the calcium acts in assisting the ferment much as hydrochloric acid in the gastric juice favours the activity of pepsin. This question is again taken up in the present investigation, and it was found possible to prepare from plasma (such as oxalate plasma which contains no ferment) a globulin which has no fibrinoplastic properties, which, however, after contact with calcium chloride, is converted into the ferment. The zymogen yields an ash containing little or no calcium, whilst the ferment is rich in calcium. The material in question arises from the formed elements of the blood, and is identical with what is called cell-globulin by Halliburton (Abstr., 1888, 974).

Fibrin, moreover, is a calcium compound, and the main action of the ferment appears to be to transfer the calcium to the fibrinogen.

Granting this hypothesis, it is possible to explain several facts hitherto but little understood in connection with blood coagulation, and to reconcile certain conflicting theories. The action of oxalates in hindering coagulation is explained on the supposition that the precipitate of calcium oxalate, on account of its insolubility, is not available for the conversion of zymogen into ferment. The action of neutral salts in restraining clotting is explained on the assumption that the ferment is a globulin, and, although the amount of salt added is not sufficient to precipitate the globulin, yet it is sufficient to lessen those intramolecular movements which, in the end, produce its specific action.

The action of peptone in hindering coagulation can be explained by the affinity between peptone and calcium compounds. It thus prevents these from converting the zymogen into the ferment. This view is supported by the fact that other substances, like soaps, which combine with calcium compounds, produce similar symptoms to those set up by peptone (Munk). Thus, there is loss of coagulability of the blood, low blood pressure, suppression of secretions, and even death. The toxic effects appear to be due to the removal of calcium salts, which are necessary, as Ringer has shown, for all vital processes. A further support to the theory is obtained from the fact that injection into the circulation of calcium chloride simultaneously with the peptone, or after the peptone, obviates the poisonous effects of the latter; peptone is then no longer capable of rendering the blood uncoagulable. Peptone also restrains coagulation in intravascular plasma (or solutions of Hammarsten's fibrinogen), provided that it is added so rapidly that the zymogen has not had time to combine with

the calcium to form the ferment. After the ferment has been once formed in the plasma, or added to the solution of fibrinogen, peptone has no longer any hindering influence on coagulation.

Wooldridge's tissue fibrinogens appear to consist of proteïd, nucleïn, and lecithin. They contain no fibrin ferment until they have been digested for some time with a little calcium chloride; it is, therefore, considered that they contain the zymogen of fibrin ferment, and their action in producing intravascular coagulation is explicable on the theory that, in the blood, they come into contact with calcium compounds, so that the zymogen is then converted into the ferment.

W. D. H.

Hematic Glycolysis. Estimation of Glycogen in the Blood. By R. Lépine and Barral (*Compt. rend.*, **112**, 1414—1416).—The sugar present in the blood of a starving dog was estimated after destroying the glycolytic ferment at 90°. Four portions of the same blood were maintained at 39° for 15, 30, 45, and 60 minutes respectively.

Taking the initial sugar at 100, the sugar present at each interval would be represented by 88, 81, 76, and 72, indicating losses for each successive 15 minutes of 12, 7, 5, and 4 respectively. Treating the blood of a well-nourished dog in the same manner, the loss of sugar for the first 15 minutes was hardly measurable. There is frequently an augmentation of the quantity of sugar present after the first 15 minutes; this is more frequently the case with serum. The glycolytic ferment is contained in the white corpuscles and not in the serum. Sugar is doubtless produced at the expense of the glycogenic matter. To estimate the amount thus formed, blood is raised to 58° to destroy the glycolytic ferment and the sugar titrated as above, yielding for successive periods of 15 minutes, a gain of 18, 2, 0, and 0 respectively. The addition of saliva to the blood did not increase the gain.

The glycolytic power of the blood of a starving dog is given by deducting the quantity of sugar obtained after an hour at 39° from the initial quantity, the apparent power only is given for the blood of a well-fed dog; to obtain the real power in the latter case, it is necessary to add the quantity of sugar produced during the same time to the apparent glycolytic power. At 58°, the transformation of glycogen into sugar is rapid; after an hour at this temperature, the whole of the glycogen of the blood may be estimated as sugar.

W. T.

Mechanism of the Production of Urea in the Animal Organism. By Popoff (*Bull. Soc. Chem.* [3], **5**, 551—554).—To determine whether the transformation of ammonium salts into urea is effected by an unorganised ferment, or by the living cell, portions of liver, spleen, and kidney, removed from recently-killed dogs and guinea-pigs, were digested, with antiseptic precautions, for many hours with warm, dilute (0·5—1·0 per cent.), sterilised solutions of various ammonium salts. In no case was any trace of urea formed. The author concludes, therefore, that the formation of urea from

ammonium salts is due to the direct action of the living cells of the various organs, and not to that of soluble ferments secreted by them.

Jn. W.

The Action of Azoimide on Living Organisms. By O. Loew (*Ber.*, **24**, 2947—2953).—Experiments were made to test the action of azoimide (N_3H) on living plants and animals. Sodium azoimide was found to be a powerful poison in all cases; seedlings died in about three days if attempts were made to grow them in a nutritive fluid containing 0·1 per cent. of the poison. Algæ were not affected so readily, but did not grow. Bacteria were killed, and thus the material in question acts as an antiseptic. Experiments with yeast, penicillium, and other fungi were entirely confirmatory of the above. To animal life, as tested on infusiorians, various invertebrates, and mammals (mice and rabbits) this substance is equally inimical. There is, first, loss of movement, preceded in mammals by muscular twitchings and finally death.

The imide is thus not available as a nitrogenous food; and the cause of its toxicity is considered to be its sudden decomposition when it comes into relation with the cells and the aldehyde containing radicles of proteïd within them. This, occurring within the nerve cells, produces first, stimulation, hence the spasmodic movements, and then kills them. Probably the decomposition that occurs, may be represented thus, $N_3H + H_2O = N_2O + NH_3$. It certainly yields ammonia when acted on by platinum black.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A Bacterium which Ferments Starch and Produces Amyl Alcohol. By L. Perdrix (*Chem. Centr.*, 1891, ii, 252—253; from *Ann. Inst. Pasteur*, 1891, No. 5).—The author has separated from Paris water a bacillus, *B. amylozymicus*, which ferments starch, with production of amyl alcohol. It is separated by cultivation on potatoes, and finally on gelatin. The bacillus is 2—3 μ long, and 0·5 μ thick; the rods are joined in pairs and chains, and in the absence of oxygen are motile, like *Vibrio butyricus*, Pasteur. The rods are readily stained; the spores are set free through the dissolution of the walls of the mother cell. The bacillus flourishes only in the absence of oxygen, readily, however, either in a vacuum or in hydrogen, nitrogen, or carbonic anhydride. The optimum temperature is 35°; it grows quite well at 20—25°; at 16—17°, fermentation commences at the end of four days. Its "maximum" temperature is 42—43°. It will grow in all the usual cultivating media, ferments the sugars and starch, but does not attack cellulose or calcium lactate, differing in this respect from *Vibrio butyricus*, Pasteur. Acids are produced during the fermentations which it causes, and the presence of acidity, equivalent to 0·055 gram sulphuric anhydride, or of

alkali equivalent to 0·08—0·11 gram in 100 c.c., is sufficient to arrest the process; the addition of calcium carbonate to the liquid enables the fermentation to become perfect. Glucose ferments to hydrogen, carbonic anhydride, acetic and butyric acids during the first three days; from the third to the ninth day, no acetic acid is formed. From saccharose and lactose, acetic acid is formed during the first five days. The greater the amount of oxygen present, the more acetic acid is produced; it was also observed that at the time of the butyric acid formation, all the cells contained spores. From the fermentation of starch a distillate was obtained, of which one-third was amyl alcohol, and from 100 grams of potatoes, 2·3—2·5 c.c. of alcohols were separated. The sugar obtained from starch is very similar to glucose, but has a less rotatory action, and its phenylglucosazone melts 10° lower than that from glucose; 94 per cent. of the starch is converted into sugar, carbonic anhydride, ethyl and amyl alcohols, acetic and butyric acids, and 6 per cent. is converted into dextrin. The sugar formed by the bacillus from starch may be fermented perfectly with beer-yeast, either after sterilisation, or in the presence of the bacillus. If either the sugar obtained by fermentation of starch with this bacillus, or a sterilised mash, be fermented with a pure cultivation of yeast, no fusel oil is formed, and the author concludes that the fusel oil found in commercially prepared alcohol, is formed by the action of bacteria. The *B. amylozymicus* remains uninjured for 10 days at 50—55°. J. W. L.

Action of the Bacillus of Malignant Œdema on Carbohydrates, and on Lactic Acid. By R. Kerry and S. Fraenkel (*Monatsh.*, **12**, 350—355; compare Abstr., 1890, 1454).—When lactic acid, in the form of its calcium salt, is dissolved in bouillon containing peptone and Kemmerich's meat extract, and the solution, placed in an atmosphere of hydrogen, is inoculated with the bacillus of malignant œdema, fermentation occurs. After remaining 8—10 days, the solution contains propyl alcohol and formic and butyric acids, but no ethyl alcohol.

Milk sugar, cane sugar, and starch, in presence of substances containing the materials necessary for building up the organism, are all fermentable by the bacillus, and yield variable quantities of butyric, formic, and inactive lactic acids, and ethyl alcohol. The formation of the last-named product on long-continued anaërobic fermentation of the carbohydrates is most probably to be ascribed to a further change induced in the propyl alcohol derived from the lactic acid.

The authors have succeeded in fermenting the wood pulp obtained from fir, and have recognised the presence of volatile alcohols and fixed acids in the product; all attempts to induce decomposition in pure cellulose have, however, led to negative results. G. T. M.

Influence of Carbohydrates on the Accumulation of Asparagine in Plants. By Monteverde (*Ann. Agron.*, **17**, 376—377).—Branches of lilac, plunged in distilled water, and in 4 per cent. solution of glycerol, and kept in the dark, contained abundance of asparagine at the end of 15 days, but neither starch nor mannitol. Branches of

the same plant kept in solutions of glucose, cane sugar, or mannitol formed no asparagine in a month, but contained much starch and mannitol. Peas, vetches, and monkshood, which do not stand the dark well, were kept in the light in an atmosphere deprived of carbonic anhydride; when plunged in solutions of glucose or cane sugar, they were completely deprived of asparagine in 10 days.

J. M. H. M.

Diastase. By G. Krabbe (*Ann. Agron.*, **17**, 381).—The author believes that diastase attacks the starch of malt, not by gradual percolation through the entire mass, but by local action. Diastase is not dialysable, and the author considers its particles to consist of groups of molecules, and chains of groups too large to pass from one cell to another; it will not even traverse biscuit ware. J. M. H. M.

Quantity of Starch in the Tubercles of the Radish. By P. Lesage (*Compt. rend.*, **113**, 373—375).—The radish contains little or no starch, even when examined in different degrees of development. If watered with solutions of sodium chloride containing 1 to 20 grams per litre, starch appears in the endoderm, and also in some cases in the cortical parenchyma. The results were as follows:—No starch with pure water or water containing 1, 2, or 20 grams of salt per litre; very little starch with 3 and 5 grams per litre; a little starch with 10 grams per litre; a considerable quantity with 4 grams per litre; 20 grams of salt per litre kills the plant. In other cases the maximum amount of starch was found with proportions of salt amounting to 5 grams and 10 grams per litre. C. H. B.

Oil of Lime Seed. By C. Mueller (*Ann. Agron.*, **17**, 431—432).—The seeds of *Tilia phatyphylla*, or *grandifolia*; *T. ulmifolia*, or *parvifolia*; and *T. intermedia*, contain little starch, and about 58 per cent. of oil. It is a yellow, bland oil, resembling the best olive oil, not bitter or aromatic, and non-drying. It does not become rancid, or resinify on exposure to air. Mixed with sulphuric acid, the liquid becomes deep brown-red, and the rise in temperature is considerable. The oil solidifies under the action of nitric acid and mercury. Its soda soap crystallises from alcohol in long, yellow needles. The oil does not solidify at −21·5°. J. M. H. M.

Earth-nut Meal. By A. Emmerling (*Bied. Centr.*, **20**, 606—607).—The author has already called attention to the adulteration of food with the husks of earth-nuts. Attempts are now being made to introduce the latter, in the form of meal, as a food. The commercial product is a dirty-yellow powder with a slightly bitter taste, and contains sand. It is prepared from the outer covering of the earth-nut, but contains portions of the skin of the seeds. The analysis of six samples gave the following results:—

	Water.	Ash.	Crude protein.	Crude fibre.	Carbohydrates.	Crude fat.
Minimum..	7·26	3·83	7 64	48·87	15·88	3·46
Average ..	7·95	10·15	8·23	53·66	16·33	4·11
Maximum .	8·58	14·31	8·97	58·96	16 85	5·65

The digestibility of the proteïds was determined in two samples :—

Total proteïds, per cent.	Digestibility, per cent.	Coefficient of digestibility, per cent.
7·87	4·20	53·3
8·66	4·01	46·3

The name given to the meal is misleading, as it denotes the skin of the seed, whereas it is prepared mainly from the outer covering, the nutritive value and digestibility of which is less than that of the skin. N. H. M.

Behaviour of Strontium Tartrate with Plastered Wines. By M. Spica (*Gazzetta*, **21**, ii, 12—19).—When a wine is plastered or treated with plaster of Paris in order to preserve it, a certain amount of potassium sulphate goes into solution and may be deleterious to the health of the consumer.

Dreyfus (*Mon. vinicole*, 1890, 66) has described a method for the removal of the potassium sulphate, which consists in treating the wine with strontium tartrate. The author gives complete analyses of three samples of wines both before and after treatment with strontium tartrate, which show that the quantity of potassium sulphate is not sufficiently reduced, as from a third to a half of the salt originally present remains in the wine. The quantity of hydrogen potassium tartrate in solution is increased from less than 1 gram to between 2 and 3 grams per litre. The amount of free tartaric acid is considerably diminished, but the total acidity notably increases and the weight of ash is diminished to about one-half, whilst a quantity of strontium hydrogen tartrate varying from half a gram to more than 1 gram per litre goes into solution and may be injurious to health. The wine is also rendered somewhat insipid by the treatment.

W. J. P.

Presence of Boric Acid in Products of the Soil. By A. Gassend (*Ann. Agron.*, **17**, 352—354).—Having had his attention directed to certain samples of wine by the Custom House authorities, the author has examined a great number of samples of French, Greek, Italian, Spanish, Algerian, and Corsican wines, and finds boric acid to be a normal constituent of them all, in the proportion of 5—10 milligrams per litre. In this proportion the ash of 10 c.c. of wine will not give the green flame with alcohol and sulphuric acid, but the boric acid is easily recognised by the turmeric paper test and by the spectroscope. When the spectroscope is employed, the ash should be moistened with 10 drops of pure hydrofluosilicic acid. The author finds similar traces of boric acid in grapes, apples, potatoes, radishes, lettuce, and in some pears, not in all. He does not find it in tea, saffron, or cow's milk. Hotter also has found boric acid in some plants. J. M. H. M.

Action of Lime as a Manure, with special regard to Paddy Fields. By O. Kellner, H. Sakano, D. Sato, and S. Shinjo (*Imp.*

Univ. Coll. Agric. Tokyo Bull, **9**, 1891, 1—25).—The excessive amount of lime (11360 kilos. per hectare) applied to rice in the paddy fields in many districts of Japan causes injury to the soil and crops. The mineral constituents of the soil are liable to become cemented together, either at the surface or a few feet below, rendering the treatment and cultivation of the soil difficult for this reason, as well as owing to the consequent stagnation of water on it. Potash and ammonia are, moreover, liberated from the soil and are liable to be washed away by the irrigating water; in fact, complete infertility from over-liming has occurred in several parts. Besides the injurious effect on the soil, both physicially and from loss of valuable constituents, the crop itself suffers, the stems becoming more fragile and the grain acquiring an inferior taste and lustre, and becoming lighter. An examination of several samples of hulled rice (all exceedingly brittle) from different soils showed no great difference in composition from ordinary hulled rice, grown without lime; but it proved to be somewhat poor in crude proteïds. This result was unexpected, as it was thought that something in the composition of the seed, as in the amount of carbohydrates, would throw some light on the action of lime. Lower percentage of proteïds has already been thought to be the reason of the glassy condition of barley and wheat, but this has never been known to arise from over-liming. Experiments made to ascertain the relation of the hardness of the grain to the percentage of crude proteïn in the dry matter showed that the proportion of nitrogenous compounds plays an important part in the resistibility of rice grains to pressure or impact. The brittleness caused by over-liming, is due to the destruction of nitrogenous matter in the soil by the lime. The mealy condition of the rice may be diminished by early cutting. The liming of over-limed fields should be stopped and large amounts of nitrogenous manure applied for the first year to compensate for the loss of nitrogen; and the manures should be thoroughly fermented before being mixed with the soil. Paddy rice prefers ammonia as nitrogenous food, and does not thrive well, as long as it is irrigated, if supplied with nitrates alone.

In order to investigate the action of lime on soils, experiments were made in which several kilograms of dry and paddy earth, after being dried and mixed, were treated with slaked lime and kept in closed bottles. The dry land soil (containing 200 grams of dry matter) was previously mixed with air-dry soy beans (containing 10 grams of dry matter) and 50 c.c. of water. The paddy soil was similarly treated, but had 300 c.c. of water. The amount of lime added corresponded with 10 grams of CaO. The results, which are given in tables, show that lime accelerates the decomposition of organic matter in both dry-land and irrigated soils, and that the action is much greater in dry land than in irrigated land. Thus, whilst the dry-land soil lost, in six weeks, 13·58 per cent. of its organic matter, the paddy soil lost only 5·85 per cent.; the same soils, but without the addition of lime, lost respectively 3·24 and 2·21 per cent. of their organic matter.

Experiments are next described which were made on the formation of nitric acid and ammonia from nitrogenous manures in dry-land and

paddy soils. The percentage composition of the partly dried soils was as follows :—

	Hygroscopic water.	Humus and combined water.	Total nitrogen.	Nitric acid.	Ammonia.	Organic nitrogen.
Dry-land soil..	41·12	14·06	0·231	0·098	0·009	0·198
Paddy soil	42·12	21·61	0·455	0·048	0·024	0·418

Glass jars were filled with the soils (1400—1600 grams), which were only so far dried as not to destroy the micro-organisms contained in them. The soils were manured with ammonium sulphate, fish manure, and in some cases with calcium carbonate, and the jars then taken to the respective fields, where they were let into the ground; the paddy soil was watered with distilled water, the level of which was kept about 2 cm. above the surface of the soil. It was found that in dry-land soil the nitrogenous manures were quickly converted into nitric acid, whilst nitrification did not take place in the irrigated paddy soil, in which ammonia seems to be among the principal products of the decomposition of the nitrogenous organic manure. The application of lime distinctly favours, on the one hand, nitrification in the dry land, and, on the other hand, the formation of ammonia in the paddy soil. The fact that nitrification does not take place in paddy soils was observed by Kellner and Sawano in 1882 (Abstr., 1884, 674; compare Baumann, Abstr., 1887, 82, and Muntz, Abstr., 1890, 1183). Many organic and inorganic constituents of soils have the power of retaining ammonia, and protect it very well from being washed away, but lime (as oxide or hydroxide) will disperse the ammonia, and may thus give rise to considerable loss of nitrogen.

The action of lime on the phosphates in the two soils was next investigated. The first soil was taken from the surface of the paddy field; the other was from the subsoil of a dry-land field. Bottles were filled with the soils (10 grams each) containing 0·0, 0·25, 0·5, 1·0, 2·5, and 5·0 per cent. of quicklime. Each bottle received 20 c.c. of water, and two weeks later a solution of potassium dihydrogen phosphate (containing 0·05 gram of phosphoric acid) was added to each bottle. The first set of soils examined one month after the application of the phosphate showed that in the paddy soil only 12·7 per cent. of the phosphoric acid remained in the soluble form, and that the addition of lime was decidedly beneficial, the maximum effect being obtained with an application of 1 to 2·5 per cent., the amount of soluble phosphate being in both these cases 22·6 per cent. of the total phosphate added. After two months, there was still more soluble phosphate (27·2 per cent.) in the soil which had 2·5 per cent. of lime. This slight after-effect is attributed to the action of calcium hydrogen carbonate on ferric phosphate, converting a part of it into free ferric hydroxide and calcium phosphate. This view is verified by direct experiments with ferric phosphate and lime-water saturated with carbonic anhydride.

The beneficial effect of lime was not observed in the case of the dry-field subsoil, and inasmuch as the two soils have the same geological origin there is no doubt that the humus of the paddy soil

played an important part in bringing about the action of lime on superphosphates.

With regard to the frequent application of large amounts of lime it is shown that the exhaustive action of lime is not confined to nitrogen and potash but also favours the consumption of the phosphatic ingredients of the soil by the crops. N. H. M.

The Value of Animal Débris as Nitrogenous Dressing. By A. Müntz and A. C. Girard (*Compt. rend.*, **112**, 1458—1460).—Nitrogenous materials require that their nitrogen be transformed into the state of nitrate before plants can avail themselves of them as aliment. Hence the aptitude of organic manures to undergo nitrification under the influence of organisms present in the soil may be taken as a measure of their activity as dressings. No practical value can be assigned to the ordinary laboratory methods of comparing the relative values of animal manures.

A number of substances have been compared by the authors by ascertaining the proportion of nitrate formed in a given time by introducing quantities of the substances containing an equivalent amount of nitrogen into a nitrifying soil and maintaining the same conditions in each case.

Commercial manures may be divided into three classes: the first, undergoing nitrification rapidly, comprises dried blood, dried flesh, horn refuse, and guano; these substances are nearly as active, and have nearly the same effect on the crop, as the mineral manures, sodium nitrate and ammonium sulphate; the second comprises burnt leather, woollen waste, and dried night soil, of which the nitrification is slower; these consequently do not give their whole effect in one season, but have some influence on the following crop; the third includes unburnt leather waste, the nitrification of which is so slow that the yield of the crop is not sensibly augmented.

This classification has been confirmed by careful practical agricultural experiments. With manures of the first class, 60 per cent. of the nitrogen has been utilised in two years; with those of the second class, 40 per cent.; and with that in the third class, 20 per cent. only. The unburnt leather refuse should only be used in compost heaps, as its nitrification proceeds too slowly for it to be directly available for the crops.

The unit of weight of nitrogen often costs more when purchased as organic manure than when obtained as saline manures; it would be more logical to pay the higher price for it in the latter case, as it could then be immediately utilised, and its application regulated according to the needs of the crops. W. T.

Analytical Chemistry.

Estimation of Hydrochloric Acid in the Gastric Juice. By J. Boas (*Chem. Centr.*, 1891, ii, 357; from *Centr. med. Wiss.*, 1891, 509).—The author has adopted Bourget's method (evaporation and incineration with barium carbonate, extraction with water, and precipitation of the barium chloride formed by sodium carbonate), with the slight modification that, after dissolving the precipitate in decinormal acid, the liquid is boiled until all carbonic anhydride is expelled, and the excess of acid is then neutralised with decinormal alkali; the indicator is phenolphthaleïn. J. W. L.

Estimation of Free Oxygen by means of Nitric Oxide. By L. L. de Koninck (*Zeit. ang. Chem.*, 1891, 78—80).—The author's attention was drawn to an article by Wanklyn and Cooper on the estimation of oxygen by means of nitric oxide. These chemists consider that this process, which was originated by Priestley, but which now only possesses an historical interest, is not only very accurate but even one of the best methods known, and they communicated a few satisfactory test analyses. The author some time ago had occasion to try the process, but his experience agreed with the results obtained by Berthelot, Lunge, and Winkler, which were very irregular and unsatisfactory. He therefore thought it advisable to once more thoroughly investigate the matter.

The *modus operandi* was practically identical with that employed by Wanklyn and Cooper, except, perhaps, as regards the preparation of the nitric oxide, which was obtained by the action of nitric acid (sp. gr. 1·1) on a spiral of sheet-copper contained in an old-fashioned Hempel's hydrogen pipette. On account of its simplicity and easy execution, the following plan was adopted :—The gas (oxygen or air) was introduced into a Winkler-Hempel burette, the nitric oxide introduced into a like apparatus, and thoroughly shaken with the water to saturate this with the gas, and also to remove traces of nitric peroxide. After a few minutes rest, the two volumes of gas were respectively recorded, and after connecting the two burettes with a capillary tube filled with water, the oxygen mixture was forced into the nitric oxide (not the reverse way), and the burettes were now disconnected. After thoroughly shaking to facilitate the absorption, and waiting for twelve or fifteen minutes, the volume of the gas was read off with the usual precautions, and the contraction noted. The results obtained once more proved the process to be absolutely useless, as the quantity of oxygen found varied between 77·5 and 122·5 per cent. of the amount operated on. From a scientific point of view, however, the results were not uninteresting.

The ratio between the volume of the oxygen and the contraction after the action of the nitric oxide may theoretically vary between 1 : 2·33 and 1 : 5, as shown by the following equations :—

$4NO + 3O_2 + 2H_2O = 4HNO$; ratio, 1 : 2·33,
$2NO + O_2 + H_2O = HNO_2 + HON_3$; „ 1 : 3,
$4NO + 2O_2 + H_2O = 4HNO$ „ 1 : 5.

A good deal depends on the celerity with which the gases have been mixed and shaken with the water. As a rule, a large excess of nitric oxide or admixture with an inert gas, such as nitrogen, seems to favour the formation of nitrous acid. L. DE K.

Estimation of Free Oxygen dissolved in Water. By W. KISCH (*Zeit. ang. Chem.*, 1891, 105—108).—The author compared the various processes in use for the estimation of free oxygen in water. (*a.*) Bunsen-Tiemann's process.—The water is boiled, and the gases collected over hot solution of caustic potash. The oxygen is then estimated by explosion with hydrogen or by absorption with alkaline pyrogallol. (*b.*) Mohr's process.—The sample is mixed with an acid solution of ferrous sulphate of known strength, then with aqueous soda to throw down the ferrous hydroxide. After remaining for a few hours (air, of course being rigidly excluded), the precipitate is redissolved in sulphuric acid, and the ferrous sulphate titrated with permanganate. (*c.*) The Schützenberger-Risler process.—The water is allowed to act on a solution of sodium hydrindigotin-disulphonate, which then passes into the blue compound. Standard solution of sodium hyposulphite is then run in till the liquid is again decolorised. (*d.*) Winkler's process.—The water is mixed with a solution of manganous chloride, and then with potassium iodide and potassium hydroxide. The precipitated manganous hydroxide rapidly absorbs the oxygen, and passes into a higher oxidised state. On adding hydrochloric acid, iodine is liberated, which is then estimated by a solution of sodium thiosulphate. On applying these processes to the same sample of water, the results obtained by Bunsen-Tiemann's process were decidedly lower than those obtained by Winkler's process, whilst those obtained by both Mohr's and the Schützenberger-Risler methods corresponded very well with Winkler's figures. The author, however, strongly recommends the latter process as being the safest, most trustworthy, and the easiest in manipulation. L. DE K.

Schützenberger's Process for the Estimation of Free Oxygen. By T. KÖNIG (*Zeit. ang. Chem.*, 1891, **108**, 110).—The author, not always getting satisfactory results with this process, investigated the cause. Success depends in a great measure on the quality of the indigo solution employed. If the sample is poor in quality, it does not absorb the oxygen rapidly enough, and a portion of this is swept away by the current of hydrogen. Indigo-carmine is obtained by precipitating a solution of purified indigo in sulphuric acid with salt. If simply collected, a pasty mass is obtained which forms the commercial indigo-carmine; but, if well washed and dried, solid sodium indigodisulphonate is obtained. These preparations vary, however, considerably in strength, sometimes from 79·08 to 91·58 per cent. in the so-called crystallised and sublimed product, whilst other

samples varied in strength from 9·41 to 72·42 per cent. It is no use to increase the quantity of indigo solution when dealing with poor samples. The colour will generally be very dirty, and it will be almost impossible to notice the change from blue to a yellow or pale yellow. Analysts wishing to use the process must, therefore, get the best quality of indigo-carmine. L. DE K.

Analysis of Phosphates. By R. JONES (*Zeit. ang. Chem.*, 1891, 3—4).—The author is very satisfied with Glaser's alcohol process, but thinks it may be much improved by lessening the amount of sulphuric acid. Glaser recommends 45 grams of the strongest acid; but even if the sample consisted solely of calcium oxide, 2 grams would be quite sufficient. The author also thinks that the quantity of the sample actually used for the analysis (0·4 gram) is far too small, and that at least 1 gram should be taken. He finally recommends the following process:—

10 grams of the sample, which must be free from organic matter, is dissolved in nitro-hydrochloric acid, and diluted to 500 c.c. 50 c.c. of the solution (= 1 gram of the sample) is evaporated to 25 c.c. and, while still hot, mixed with 10 c.c. of dilute sulphuric acid (1 : 5). After adding 150 c.c. of alcohol, the mixture is allowed to remain for at least three hours (Glaser thought half an hour sufficient). The calcium sulphate is collected and washed with alcohol until the washings, after being diluted with water, do not show the faintest acidity with methyl-orange. If it is desired to estimate the amount of calcium (the process is really devised for the accurate estimation of the iron and aluminium), the filter is put into a platinum dish, the alcohol burnt off, and the calcium sulphate finally ignited and weighed. The alcoholic filtrate is distilled, the residue rinsed into a beaker, and a slight excess of ammonia added, but it must again be completely boiled off. This is of particular importance when the phosphate contains magnesia; the precipitate at first always contains magnesia, but this is redissolved on boiling. In order to get a clear filtrate, it is as well to wash the precipitate, consisting of ferric and aluminic phosphates, with water containing a little ammonium nitrate. If it is preferred to weigh the iron and aluminium as pure oxides, the precipitate may be treated according to Stutzer's plan, namely, removal of the phosphoric acid by ammonium molybdate and precipitation of the filtrate with ammonia. L. DE K.

Physiological Detection of Carbonic Oxide in a Medium containing only 1 part in 10,000. By N. GRÉHANT (*Compt. rend.*, **113**, 289—290).—When air containing only 1 part of carbonic oxide in 10,000 is passed for half an hour through 50 c.c. of defibrinated, filtered dog's blood, the respiratory power falls from 23·7 to 23·0. Under a pressure of 5 atmospheres, with the same gas and the same blood, the respiratory power falls to 17·2. This fact may be utilised for the detection of minute quantities of carbonic oxide. It is clear that the absorption of carbonic oxide by the blood is not determined by the percentage of this gas by volume, but by the mass of the gas present in a given volume. C. H. B.

Separation of Barium from Calcium. By R. Fresenius (*Zeit. anal. Chem.*, **30**, 583—595).—*Methods based on the Differential Action of Alkaline Carbonates on the mixed Sulphates.*—Boiling the freshly-precipitated sulphates with a mixture of potassium carbonate and sulphate, and subsequent treatment with hydrochloric acid, gives fairly accurate results, the comparatively small errors compensating one another. The errors are much larger when cold ammonium carbonate solution is used for the decomposition of the calcium sulphate, the barium sulphate being also attacked to a considerable extent, whilst weighable amounts of calcium are left undissolved. Fleischer's method gives results sufficiently accurate for most purposes. The solution is precipitated by a mixture of 3 parts of potassium sulphate and 1 part of potassium carbonate. Since this at once throws down the calcium as carbonate, there is no tendency for the barium sulphate to retain calcium sulphate. After 12 hours' digestion, the precipitate is washed with ammonium carbonate, then dried, weighed (burning the filter and treating the ash with ammonium carbonate), and treated with a measured excess of standard hydrochloric acid, the excess being titrated with alkali. To complete the action of the acid on the calcium carbonate, prolonged digestion is necessary. Sidersky's process likewise affords serviceable results. The solution is precipitated by a mixture of ammonium sulphate and oxalate (200 grams of the former and 30 grams of the latter in a litre). The washed precipitate, consisting of barium sulphate and calcium oxalate, is dissolved in dilute hydrochloric acid, and the oxalic acid titrated by permanganate. The barium sulphate can then be collected (after partially neutralising the acid by ammonia), or the joint amount of the two metals may be found in a separate portion. Rose's proposal to separate calcium sulphate from strontium sulphate by digestion with concentrated solution of ammonium sulphate, appeared likely to succeed with a mixture of barium and calcium sulphates, but prolonged digestion leaves much of the calcium undissolved, whilst the portion dissolved cannot be accurately estimated by ammonium oxalate, since the ammonium sulphate solution (whether concentrated or dilute) is capable of dissolving a very notable amount of calcium oxalate. M. J. S.

Combination of Wet and Dry Methods in Chemical Analysis. By W. E. Adeney and T. A. Shegog (*Chem. News*, **64**, 174—175, 185—187, and 192—193).—The problems which the authors wished to solve by direct experiments were: 1. Whether, when fused in the reducing flame on charcoal with borax and sodium carbonate, the metals antimony, tin, lead, arsenic, silver, bismuth, copper, nickel, and zinc could be completely reduced from their salts containing either volatile or non-volatile acids. 2. Whether, when similarly treated, aluminium, chromium, manganese, cobalt, and iron are wholly non-reducible from their compounds; the cobalt and iron more especially from their arsenates and phosphates. 3. Whether, when a mixture of salts is similarly treated, the constituent metals thereof respectively behave as in simple compounds, or whether their behaviour is modified in any way. In their present paper, the authors mainly deal with the

problems Nos. 1 and 2. The details of manipulation are as follows:—

The Charcoal Support.—The pieces should be about 15 inches in length, and about $1\frac{3}{4}$ inches in diameter, and should be tolerably free from fissures. The cavity into which the substance is to be introduced should be bored conical, the sides being slightly curved. The size, of course, varies with the quantities of the materials used in the experiment; but, in the authors' assays, the diameter was $1\frac{1}{2}$ inches, and the greatest depth $1\frac{1}{2}$ inches. *The Source of Heat.*—Although an ordinary paraffin oil lamp, or one burning solid paraffin, may be advantageously used, still, when coal gas is procurable, it is by far the most convenient source of heat, as it can be burnt at the end of a flattened tube; and, if this be pivoted so that it can rotate in a vertical plane, it will be found of advantage in dealing with readily oxidisable metallic beads. *The blowpipe* used was an ordinary mouth-blowpipe, furnished with a platinum jet, and fixed in a clip on a retort-stand. An india-rubber hand-blower was used for obtaining the blast. *The borax* used was fused in a platinum dish, powdered, and kept in a dry and well-stoppered bottle. *The silver* was at first used in the form of nitrate, but, this not answering well, it was replaced by a mixture of argentic chloride and borax. In some cases it was used in the form of wire, or a button, after the substance and the fluxes had been first fused in the oxidising flame. *The sodium carbonate*, which the authors now only employ in the analysis of silicates, was the ordinary dried and powdered commercial article. *Quantities.*—The most convenient quantities to work on generally are 0·3 gram of substance and 1·2 grams of borax; but, when dealing with ores rich in nickel or zinc, not more than 0·1 gram should be taken. While the fusion is proceeding, the charge must be worked round and round the cavity, the metallic bead being made to run round the glass and pick up the metals as reduced. To prevent oxidation, a stream of coal gas is directed into the cavity while the melt is cooling.

As regards the first problem, the authors found that when fusing oxygenated compounds of antimony, tin, lead, arsenic, bismuth, and copper, or nickel chloride (mixed with metallic arsenic), with a mixture of borax, sodium carbonate, and argentic chloride, the reduction of the metals was practically complete, the glass bead being free from metal. Zinc, however, was found in both beads, showing the incompleteness of the reduction. Another series of experiments was now made. The ores and fluxes were fused together in a shallow cavity in charcoal with the aid of the oxidising flame. After cooling, the beads were transferred to a cavity of the usual shape and size, and, after the addition of a button of metallic silver, heated in the reducing flame. Satisfactory results were obtained with antimony, lead, arsenic, copper, and nickel; but in the case of tin and bismuth the reduction was incomplete.

As regards the difficultly reducible metallic oxides, the authors operated as follows:—0·3 gram of the substance was fused with 1·2 grams of borax or charcoal in the oxidising flame, 0·9 gram of silver button (1·2 grams when dealing with cobalt) was added, and the fusion

repeated in the oxidation flame. The results were qualitatively satisfactory with cobalt, aluminium, chromium, and manganese; of iron, only a mere trace passed into the silver button.

The investigation as regards mixed metallic compounds will be carried on by one of the authors. L. DE K.

Assay of Commercial Aluminium. By F. REGELSBERGER (*Zeit. ang. Chem.*, 1891, 20, 52).—Klemp has proposed to measure the volume of hydrogen which is evolved by dissolving the metal in potash-ley; but as commercial aluminium invariably contains silicon, which also evolves hydrogen, his process cannot give the exact amount of pure metal. A sample submitted to the author contained 98 per cent. of aluminium, but as it also contained 1·5 per cent. of silicon, it showed 99·9 per cent. of metal by Klemp's process. The author thinks it by far the best plan to carefully estimate the percentage of impurities in the sample and take the aluminium by difference; but if a direct estimation of the metal is desired, he proceeds as follows:—

Two grams of the sample is dissolved in a platinum basin, in water containing 15 grams of potassium hydroxide, and the whole is finally made up to 200 c.c. 50 c.c. of the alkaline solution (= 0·5 gram of the sample) is now boiled with a slight excess of neutral ammonium nitrate which throws down the alumina with more or less silica. After washing, igniting, and weighing, any silica must be estimated in the usual way by fusion with potassium hydrogen sulphate, and if there is any reason to believe that the reagents used contain alumina or silica, the usual check must be made. L. DE K.

Direct Estimation of Aluminium in Iron and Steel. By T. M. DROWN and A. G. MCKENNA (*Chem. News*, **64**, 194—196).—The alumina obtained during a quantitative analysis often contains ferric oxide and phosphoric acid. As the direct estimation of the alumina is as yet very unsatisfactory, the analyst, as a rule, contents himself with estimating the iron and phosphoric acid, and taking the alumina by difference. This is a very good plan when the iron and phosphorus are present in relatively small quantities, but when, as in the modern alloys of aluminium and iron, the aluminium may be present only to the extent of a fraction of ·1 per cent., nothing short of the isolation of the alumina can satisfactorily prove its presence. The authors, after many experiments, finally adopted the following electrolytic process:—About 5 to 10 grams of the iron or steel is dissolved in sulphuric acid, and the solution heated until white fumes of sulphuric anhydride begin to come off. Boiling water is added to dissolve the iron salt, and the liquid filtered off from the silica and carbon, which are washed with acidified water. The filtrate is nearly neutralised with ammonia, and, if necessary, diluted to 300—500 c.c. The beaker in which the electrolysis is to be made contains from 500 to 1000 grams of mercury, which constitutes the cathode. It is connected with the battery or dynamo current in such a manner that about 2 ampères may pass through the

solution over night, which is best accomplished by using three lamps of 32-candle power, arranged in parallel on an Edison circuit. After, as far as possible, neutralising the acid which has been set free, the electrolysis is continued until the liquid gives no reaction for iron. It generally turns reddish from the formation of permanganic acid. When all the iron has amalgamated, the liquid is removed by means of a pipette while the current is still passing, and the mercury is repeatedly washed. The platinum anode, which will generally be slightly coated with manganese dioxide, is now taken out, and the mercury again washed with water until the last traces of solution have been removed from it. After filtering to remove any suspended manganese dioxide, excess of sodium phosphate is added, and also 10 grams of sodium acetate. After boiling for at least 40 minutes, the aluminium phosphate is collected, washed, ignited, and weighed. The formula is not, as generally believed, $Al_2P_2O_8$, but $7Al_2O_3,6P_2O_5$. It should, of course, have a pure white colour, but it must be remembered that the presence of even 4 per cent. of ferric oxide will give a decidedly reddish product. In case of doubt, it may be fused with potassium hydrogen sulphate, and the solution once more submitted to electrolysis, but the authors have always found this to be superfluous.

The test analyses are satisfactory. L. DE K.

Separation of Iron from Cobalt, Nickel, and Manganese. By A. C. CAMPBELL (*Zeit. anal. Chem.*, **30**, 616—617; from *J. anal. Chem.*, **2**, 291).—Ferric salts are precipitated by lead carbonate, whilst those of cobalt, nickel, manganese, and ferrous iron are not decomposed. Some lead chloride should be present to neutralise any traces of alkali. Warming promotes the reaction, and as oxidation of the cobaltous, manganous, and ferrous salts must be prevented, nitrates should be absent. The washed precipitate is treated with sulphuric acid, whereby the iron is redissolved and separated from the lead. To test the iron precipitate for cobalt and nickel, it is dissolved in hydrochloric acid and the concentrated solution reduced by tin foil. Traces of cobalt or nickel can then be recognised by the colour they communicate to the colourless ferrous chloride solution.

M. J. S.

New Methods of Quantitative Analysis. Part I. By A. BAUMANN (*Zeit. ang. Chem.*, 1891, 135—142).—When chromic acid is dissolved in dilute sulphuric acid and mixed with hydrogen peroxide, oxygen is evolved. According to some investigators, the reaction is not quantitative, but the author's experiments prove that 1 mol. of chromic acid liberates exactly 2 mols. of oxygen and 1 mol. of potassium dichromate 4 mols. of that gas. The most suitable apparatus is a Wagner's azotometer, or a Knop's apparatus connected with a Wagner's gas flask, which is an ordinary flask into which a small glass cylinder has been sealed.

Estimation of Chromic Acid.—The liquid, which must not be too concentrated and not exceed 50 c.c. in bulk, is mixed with 10 c.c. of dilute sulphuric acid (1 : 5) in the outer chamber of the flask. The

little glass cylinder is filled with 5 to 10 c.c. of commercial hydrogen peroxide. After allowing the hydrogen peroxide to run into the chromate, the liquid will at first assume a fine blue colour, and then gradually evolve oxygen. The bulk of this gas will be given off in a few minutes, but the remainder will be only expelled after five minutes' brisk agitation. When shaking, the operator must open the stopcock about every half minute to let the oxygen gradually escape into the measuring tube. The liquid in the non-graduated tube ought to stand a little lower during the evolution of the gas. When no more gas is given off, the apparatus is put, for about 15 minutes, into water of the temperature of the room; the water in the tubes is levelled, and the volume of the gas is read off; 1 c.c. of oxygen at normal temperature and pressure = 0·002246 gram of chromic acid (CrO_3). It is not advisable to work with hydrochloric instead of sulphuric acid, as there is always a risk of chlorine being evolved. Traces of free nitric acid do not interfere, but when the liquid contains more than 0·2 gram the oxygen found will be somewhat too low. Acetic and succinic acids do not affect the results, but other organic acids or organic substances decidedly interfere. In standardising a solution of potassium dichromate, it must be remembered that only three-eighths of the oxygen evolved is derived from the chromic acid.

Estimation of Chromic Oxide.—This is very readily converted into a chromate by treating its alkaline solution with hydrogen peroxide, the excess of which may be driven off by boiling. After neutralising the solution with sulphuric acid, the chromic acid is determined as directed, and calculated to Cr_2O_3. In the assay of chrome-iron ore by this process, the use of nitre as an oxidising flux must be avoided, and 0·3 gram of the finely powdered mineral must be fused with a mixture of 3 grams of sodium carbonate and 3 grams of barium peroxide for half an hour. The mass must afterwards be decomposed with sulphuric instead of hydrochloric acid.

Estimation of Combined Sulphuric Acid.—The liquid, which should contain no excess of hydrochloric acid and but traces of nitric acid or nitrates, is put into a 100 c.c. measuring flask, and precipitated in the cold with a solution of pure barium chromate in hydrochloric acid. As the commercial salt often contains alkali chromate, it must before use be thoroughly washed with water until the filtrate is practically colourless. The residue is then dissolved in an insufficiency of hydrochloric acid containing 3 per cent. HCl, and, after filtering, preserved for use.

After diluting with water to about 90 c.c., the liquid is rendered faintly alkaline with ammonia, made up to the mark, and filtered. An aliquot part of the filtrate, say 25 or 60 c.c., is then treated in the apparatus with sulphuric acid and hydrogen peroxide. 1 c.c. of oxygen = 0·001787636 gram of sulphuric anhydride.

The various test analyses are very satisfactory. L. DE K.

General and Physical Chemistry.

Apparent Variability of the Electro-chemical Equivalent of Copper. By J. Vanni (*Ann. Phys. Chem.* [2], **44**, 214—221).—Gray (*Phil. Mag.* [5], **22**, 389; **25**, 179), in his researches on the electro-chemical equivalent of copper, found that this magnitude at 12° varied from 0·0003287 with a current density of 20 milliampères per square centimetre at the cathode, to 0·0003278 with a density of 3·3 milliampères; and at 35° sank so low as 0·0003245. He advances as a probable explanation of this variability the fact, observed by Gore, that the solution of copper sulphate dissolves up a quantity of copper varying with different conditions. The object of the present investigation was to test the validity of this explanation, and to determine the true electro-chemical equivalent.

Two copper voltameters with plates of different surface (4 : 1) were placed in the same circuit; and it was found, for instance, that with a solution of copper sulphate containing 1 per cent. of free sulphuric acid, 0·1903 gram of copper was deposited on the larger cathode, while 0·1960 gram was deposited on the smaller cathode, in the course of three hours. After interruption of the current, the cathodes were allowed to remain three hours longer in the solutions, when it was observed that the larger cathode had lost weight to the extent of 9·2 milligrams, and the smaller cathode only 3·2 milligrams. These weights, added to the former pair, give 0·1995 gram and 0·1992 gram respectively—results sufficiently close.

The author found that when the copper sulphate solution employed contained merely a trace of sulphuric acid (about 5 milligrams per litre), there was no perceptible quantity of copper dissolved in two hours. With such solutions, the electro-chemical equivalents of copper and of silver were compared; and, taking that of silver as equal to 0·001118, the author gives, as a mean value of 12 concordant experiments, the electro-chemical equivalent of copper in cupric salts as equal to 0·0003284. J. W.

New Method of Measuring Electromotive Forces and Electrical Resistances. By S. Pagliani (*Gazzetta*, **21**, 449—454).—A standard wire of known resistance is joined in circuit with the current generator whose electromotive force is to be measured. A branch circuit containing a voltameter is also established, having one terminal fixed to one end of the standard wire and the other fixed to a key which slides along the standard wire. The voltameter consists of a glass tube, closed by two taps, containing a 25 per cent. solution of potassium iodide to which has been added a little starch solution. Platinum and copper wires are used for the cathode and anode respectively. The width of the tube is 10 mm.; the distance between the electrodes 120 mm. The resistance of the standard wires must be so great as to render negligible the internal resistance of the

current generator. At the commencement of the determination, the branch circuit is so arranged that the difference of potential at its terminals is insufficient for the electrolysis of the potassium iodide solution: the key is now moved along the standard wire until it reaches a point at which a violet coloration is observable at the surface of the platinum wire. The position of the key is then noted, and the electromotive force of the current generator can be calculated in terms of the electromotive force necessary to decompose the potassium iodide solution (0·610 volt).

Electrical resistances may be measured by employing a current generator of known electromotive force, and inserting the unknown resistance in either the main or the branch circuit.

The author states that this method gives very concordant results.

W. J. P.

Characteristic Difference between the Substituted Alcohol Radicles directly united with Carbon or with Nitrogen. By C. Matignon (*Compt. rend.*, **113**, 550—551).—In the course of a thermochemical study of the ureides, the author has arrived at the law, "The substitution of an alcohol radicle directly united with nitrogen increases the heat of combustion more than when the same radicle is directly united with carbon." The publication of a paper by Stohmann and Langbein (this vol., p. 4), enunciating the same law, rendered necessary the immediate production of the author's results.

Caffeïne, theobromine, cholestrophane, and ethylcarbamide were purified and analysed; their heats of combustion at constant pressure, together with those of parabanic acid and carbamide, are given below.

		cal.	cal.
Caffeïne(methyltheobromine)	$C_7O_2N_4H_7Me$,	1016·0	170·1.
Theobromine	$C_7O_2N_4H_8$	845·9	
Ethylcarbamide	CON_2H_3Et,	472·2	320·7
Carbamide	CON_2H_4,	151·5	(=155+165·7).
Cholestrophane	$C_3O_3N_2Me_2$,	538·6	326
Parabanic acid	$C_3O_3N_2H_2$,	212·6	(=163 × 2).

The introduction of a methyl group united with carbon never increases the heat of combustion of the substance by more than 157 cal.; in the above cases, this number is exceeded by an amount far beyond the limits of experimental error. Ethylcarbamide is considered as derived from urea by two successive methyl substitutions; taking 155 cal. as the mean for a substitution of methyl united with carbon, 165·7 cal. is the increase caused by the introduction of a methyl group combined with nitrogen.

The application of this law confirms the suggestion of Grimaux, that pyruvile is a methyl derivative of allantoïn, and that it is a true homologue of that substance; the increase in heat of combustion in this case is 153 cal.

W. T.

Expansion of Water. By W. Marek (*Ann. Phys. Chem.* [2], **44**, 171—172).—This paper contains a table of the densities of water con-

taining air for every tenth of a degree from 0° to 31°. Details of the experimental method will be given in a subsequent communication.

H. C.

Molecular Weights of Liquids as evinced by their Boiling Points. By H. M. Vernon (*Chem. News*, **64**, 54—58).—The author endeavours to show that from the boiling point of liquids some indication as to the probable value of their molecular weights may be obtained. Hydrogen iodide boils at −25°, hydrogen bromide at −73°, and hydrogen chloride at −100°, from which a boiling point of about −120° might be predicted for hydrogen fluoride. But since hydrogen fluoride actually boils at 19·4°, we must assume a more complex molecule for this substance in the liquid state than that represented by the formula HF. This result agrees with Thorpe and Hambly's conclusion that at the boiling point the hydrogen fluoride molecule is probably H_4F_4. In like manner, comparing the boiling point of water with those of the similar compounds SH_2, SeH_2, and TeH_2, which are gaseous at temperatures far below 0°, we should have to assign to liquid water a molecular weight not smaller than that corresponding with the formula $(H_2O)_4$. The following table illustrates the striking regularity in increase of boiling point which is always observed on the substitution of bromine for chlorine:—

Chloride.	B. p.	Bromide.	B. p.	Increase for each atom of Br.
PCl_3	76·0°	PBr_3	175·0°	33·0°
$POCl_3$	107·2	$POBr_3$	195·0	29·3
$AsCl_3$	134·0	$AsBr_3$	220·0	28·7
BCl_3	18·2	BBr_3	90·5	24·1
$SiCl_4$	59·6	$SiBr_4$	154·0	23·6
$CHCl_3$	61·0	$CHBr_3$	151·0	30·0
CCl_4	76·5	CBr_4	189·0	28·1
CH_3Cl	−22·0	CH_3Br	4·5	26·5
$TiCl_4$	136·1	$TiBr_4$	230·0	23·5

Other cases are discussed, and the author argues, from a study of the boiling points, that in all probability all compounds, both organic and inorganic, containing one or more hydroxyl groups, have in the liquid state molecular weights double those expressed by their ordinarily received formulæ.

H. C.

Solubility of Gases in Water. By C. Bohr and J. Bock (*Ann. Phys. Chem.* [2], **44**, 318—343).—The authors have made fresh determinations of the solubility of oxygen, hydrogen, and nitrogen in water, partly by means of a Bohr's absorptiometer, and partly by means of two new instruments—a differential absorptiometer and a pumping-out apparatus—which are fully described and figured in the paper. The differential absorptiometer was used for temperatures from 0° to 60°; from 60° to 100° the other apparatus was employed.

The mean coefficient of absorption of oxygen in water was found to

be 0·03497 at 15°; at 100° it is 0·01679. The agreement with the values obtained by Dittmar and Winckler is good. For nitrogen, the absorption coefficient is 0·01667 at 19°, and 0·01046 at 100°. The coefficient remains practically constant between 60° and 100°. The authors' numbers agree well with those of Petterson and Sondén, Dittmar, and Hamberg, but diverge considerably from those of Bunsen and of Hüfner.

In the case of hydrogen, the author finds that the coefficient of absorption is not independent of the temperature, as Bunsen stated, but falls to a minimum at about 60°, after which it rises until at the boiling point it becomes equal to the coefficient of absorption of oxygen at the same temperature. The numerical values are—

$$\alpha_{0°} = 0·0203,\ \alpha_{15°} = 0·0183,\ \alpha_{60°} = 0·0144,\ \alpha_{100°} = 0·0166.$$

The authors further made two determinations of the solubility of carbonic anhydride, and found α for 37·29° to be 0·5629, and for 100° to be 0·2438. J. W.

Nature of Solution. By J. A. Wanklyn and W. Johnstone (*Chem. News*, **64**, 39, 51, and 146; compare Abstr., 1891, 1412).—When a solid is dissolved, the volume of the solution is not, as a rule, equal to the sum of the volumes of the solid and solvent. The authors have determined the amount of the change for a considerable number of substances which dissolve in water.

The alteration, which is usually that of contraction, is expressed in terms of a quantity, which they name the *condensate*, and obtain by subtracting the mass of solvent displaced by unit mass of dissolved substance from the ratio of the excess of the density of the solution over that of the solvent to the solution-density of the dissolved substance:—

$$c = i - i_1,$$

where $i = \dfrac{\text{Density of solution} - \text{density of solvent}}{\text{No. of grams of dissolved substance per c.c. of solution}}$,

and $i_1 = 1 - \dfrac{1}{\text{Density of dissolved substance}}$.

The condensate, which, it is stated, may be regarded as the amount of solvent which enters into combination with, or is condensed by the dissolved substance, appears in several cases to bear a simple molecular ratio to the amount of the latter. Thus, with potassium nitrate, the number is 0·058, whilst the ratio $H_2O : 3KNO_3$ is 0·059 and with barium hydroxide the number is 0·320, whilst the ratio $3H_2O : Ba(OH)_2$ is 0·316. In other cases, however, the agreement is not so close, and the numbers can only be expressed by more complex ratios.

With cane sugar, the condensate is zero, whilst with certain ammonium salts it appears to be negative. Jn. W.

Strong Solutions and the Dissociation Hypothesis. By S. U. Pickering (*Ber.*, **24**, 3317—3327).—The author states that the fac

established by him (Abstr., 1891, 972), that weak solutions of sulphuric acid and other substances contain less, instead of more, acting units than the acid and water separately, cannot be brought into harmony with the dissociation hypothesis, as Arrhenius considers (Abstr., 1891, 1148), by admitting that complex aggregates of similar molecules exist in pure liquids and strong solutions. After answering some recent criticisms of Arrhenius, he gives a preliminary statement of numerous results obtained in a study of the freezing points of strong solutions. Very weak solutions of electrolytes, as is well known, exhibit an abnormally large molecular depression; this decreases as the strength is increased up to a certain point, but afterwards it again increases, and often attains values which are abnormally large in a very high degree. Non-electrolytes appear to behave in the opposite manner; in every case investigated, the molecular depression decreases with the strength of the solution, although in a few cases this abnormally small depression is preceded by a comparatively slight and temporary increase. Although so-called dissociation may offer some explanation of the behaviour of very weak solutions, it appears to be incapable of explaining that of stronger solutions, for here the molecular depression increases, while the amount of dissociation, as measured by the electric conductivity, diminishes. The abnormally high values obtained by Perkin for the magnetic rotation of many salts, &c., in strong solution, and by Gladstone for their refractive indices, is probably due to the same causes as those owing to which these solutions exhibit an abnormally large depression. A table is given in which the rotation values are compared with the amount of dissociation existing, and there appears to be no connection whatever between the two.

S. U. P.

The Cryoscopy of Cane Sugar Solutions. By S. U. Pickering (*Ber.*, **24**, 3328—3341).—Numerous determinations, both with very weak solutions, and with solutions up to 64·5 per cent., are quoted, and the results examined in detail, partially by the bent-lath method and partially by the application of parabolas deduced from the experimental values. In all the instances where both methods were applied to the same series of results, they have led to precisely the same conclusions respecting the nature of the figure formed, that is, whether it is a continuous curve or whether it contains changes of curvature. With very weak solutions—0 to 1·2 mols. to $100H_2O$, with an actual depression extending up to 1·4°—the molecular depression increases from 1·050° to 1·105° at a strength of 0·1 mol., then diminishes to 1·102 at 0·3 mol., and finally increases again till it reaches 1·156° at 1·2 mols. From 0·06 to 1·2 mols. can be represented by two curves meeting at about 0·6 mol., so as to give the apparent error of the points very nearly the same value as the known experimental error, whereas when the same portion is drawn as one continuous curve the apparent error is twice the experimental error, and there is such a bad arrangement of error of like signs, that such a drawing could not be accepted as a legitimate representation of the results. Hence the author concludes that a "break" exists at about 0·6 mol. to $100H_2O$. There appears to be some further irregularity in

the region of much weaker solutions, but the position of a break here cannot well be determined.

With the freezing points of stronger solutions, the figure is sensibly a straight line as far as about 2·5 mols.; it then bends downwards as far as 5·5 mols., when it begins to bend in the opposite direction. The molecular depression for the strongest solution, 9·5 mols., is 1·445, the maximum molecular depression being reached at 8 mols., where it amounts to 1·455. The author considers that there is a change of curvature at 2·5 or 2 mols., but not at 5·5 mols., where the inflection of the figure occurs: a representation, either by bent-lath curves or by parabolas, which shows a break at the former point, gives a mean apparent error for the points agreeing very closely with the experimental error, whereas a one-curve representation, which makes no break at this point, gives an apparent error 2·4 times larger than the known experimental error, or taking into account indications of error other than the mean error—such as arrangement of like signs into groups, and the occurrence of errors of improbable magnitude—the total apparent error, and, therefore, the improbability, of the one-curve drawing, is estimated by the author to be 100 times greater than that of the two-curve drawing. Representing the figure by three curves, instead of two, produces no appreciable diminution in the apparent error of the points. S. U. P.

Existence of Acid or Basic Salts of Monobasic Acids in very Dilute Solutions. By D. Berthelot (*Compt. rend.*, **113**, 641—643).—If a dilute solution of an alkali is added, in gradually increasing proportion, to an equivalent solution of a monobasic acid, the phenomena can be represented in a very simple manner by means of a curve, the abscissæ being the electrical conductivity of the mixture, and the ordinates the proportion of one of the constituents. The curve consists mainly of two right lines (one corresponding with excess of acid, and the other with excess of base), inclined at an acute angle, and connected by a short curved portion, part of which represents the effect of a slight excess of acid, whilst the remainder represents the influence of a slight excess of base. A slight excess of base has a greater effect than an equivalent excess of acid, but the effect disappears rapidly as the quantity of acid or base in excess is increased. These results are very distinctly shown by solutions of barium chloride, hydrochloric acid, and barium hydroxide, and they indicate that acid or basic salts are not completely decomposed by dilution, but exist in minute quantities even in very dilute solutions. C. H. B.

Catalytic Influence of Acids on the Velocity of the Reaction between Hydrogen Peroxide and Hydriodic Acid. By G. Magnanini (*Gazzetta*, **21**, 476—490).—The author has studied the effect of hydrochloric, nitric, nitro-hydrochloric, sulphuric, hydriodic, oxalic, acetic, monochloracetic, and phosphoric acids on the velocity of the reaction between hydrogen peroxide and hydriodic acid, in a similar manner to that employed in his study of the reaction between bromic and hydriodic acids (Abstr., 1891, 144). As in the case of the latter reaction, the velocity of the action is acceler-

ated by the addition of acid. When hydrochloric or sulphuric acid is employed, the accelerations are not rigorously proportional to the amount of acid added, the ratio of the acceleration to the quantity of foreign acid present decreasing slightly, but sensibly, as the amount of acid is increased; this constitutes a marked difference from the case of bromic and hydriodic acids, in which this ratio increases rapidly with increase of acid.

The quantity of iodine set free when nitric acid is used is practically the same as with hydrochloric acid. The accelerating effect of hydriodic acid is very great. W. J. P.

Optical Proof of the Existence of Suspended Matter in Flames. By G. G. Stokes (*Chem. News*, **64**, 167—168; compare G. J. Burch, Abstr., 1885, 466).—When a beam of sunlight, condensed by a lens, is passed through a candle-flame, the area of intersection of the double cone of light with the luminous envelope is marked by two brighter patches of light of inappreciable thickness, which exhibit the polarisation of light scattered by fine particles —that is to say, when viewed in a direction perpendicular to the incident light, it was polarised in a plane passing through the beam and the line of sight. They can be made more conspicuous by viewing the whole through a cell containing copper ammonium sulphate solution, or through cobalt glass. The same phenomenon is shown by a luminous gas or ether flame, but not by the blue base of a candle flame, or by a Bunsen flame, even when rendered luminous with sodium chloride, or by an alcohol flame, or by an ether flame, just expiring for want of air.

The separation of carbon, or carbon associated with hydrogen, thus rendered evident by its polarising effect on light, is due to the action on the volatile carbon compounds, in the absence of a sufficient supply of oxygen to effect complete combustion, of the heat evolved by the more complete combustion at the base of the flame. In the case of the dying ether flame, the heat is probably distributed over too large a mass of inert gases to effect the decomposition.

The thinness of the stratum of glowing carbon is probably due to the combined attack of oxygen on the outside, and carbonic anhydride on the inside (compare Smithells, Proc., 1891, 159). Jn. W.

Inorganic Chemistry.

Sulphur Tetroxide. By D. Carnegie (*Chem. News*, **64**, 158—159).—A criticism of Traube's work on the electrolysis of 40 per cent. aqueous sulphuric acid (Abstr., 1891, 978). The author, whilst admitting that the substance formed cannot be a heptoxide of sulphur, comments on the absence of direct evidence in favour of the existence of a tetroxide. The ratio 1 : 5 of active oxygen to sulphuric anhydride, which Traube considers to prove the existence of the tetroxide SO_4 in the electrolysed solution, would be equally well

explained on the hypothesis of the existence of a substance having the composition S_2O_7,H_2O_2,xH_2O. The existence of such a substance would not only accord with Berthelot's results (Abstr., 1878, 469), but would harmonise with the known existence of tungsten and molybdenum heptoxides, and with the tendency of peroxides of the type M_2O_7 to form stable compounds with hydrogen peroxide. Moissan's perchromic acid (Abstr., 1884, 20; compare Berthelot, Abstr., 1889, 350) might then be regarded as a compound, Cr_2O_7,H_2O_2,H_2O, of the same type.

With regard to the low amount of active oxygen shown by the iodometric method, the author points out that this cannot be accounted for by the presence of sodium hydrogen carbonate, since the latter has practically no action on iodine, but that it can be accounted for by the presence of free alkali in the potassium iodide, and that this supposition accords with the higher results which were obtained on working with acid instead of neutral solutions.

Jn. W.

Azoimide. By T. Curtius (*Ber.*, **24**, 3341—3349; compare Abstr., 1891, 56).—Ethereal salts of benzoic acid react with hydrazine hydrate according to the equation $Ph{\cdot}COOR + N_2H_4,H_2O = COPh{\cdot}NH{\cdot}NH_2 + ROH + H_2O$. The benzoylhydrazine, when treated with nitrous acid, yields benzoylazoimide, and on digesting this with sodium ethoxide it is decomposed quantitatively into sodium nitride, NaN_3, and ethyl benzoate.

The salts of azoimide may also be prepared from hippurylhydrazine, by the action of nitrous acid; in this case, a compound is formed which was previously termed nitrosohippurylhydrazine; it is, however, a diazo-compound with the formula $COPh{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}N{\cdot}OH$ (see below); it cannot be converted into hippurylazoimide by elimination of water, but on treatment with ammonia in alcoholic solution, it is decomposed into hippuramide and ammonium nitride; the hippuramide combines with hydrazine hydrate to form hippurylhydrazine.

Argentic nitride, AgN_3, has been previously described; it is soluble in ammonia, from which it crystallises in long, colourless needles; it is exceedingly explosive.

Mercurous nitride, HgN_3, is precipitated in microscopic needles which are insoluble in water; it is more stable than either the silver or lead salts, becomes yellow on exposure to light, and yields a black, insoluble compound with aqueous ammonia.

Plumbic nitride, PbN_6, is prepared by adding plumbic acetate to a solution of the sodium or ammonium salts; it is soluble in excess of the precipitant, but insoluble in water in the cold, and more sparingly soluble in boiling water than plumbic chloride, which it closely resembles. It crystallises from water in long, colourless, lustrous needles, which explode violently on gently warming and decompose gradually when heated with water or acetic acid.

Sodium nitride is most readily prepared in the manner described above, but may also be obtained by adding soda to solution of the free acid or of the ammonium salt; it is readily soluble in water, insoluble in alcohol or ether, has a slight alkaline reaction and a

saline taste. The compound is neither volatile nor hygroscopic; its solution may be evaporated to dryness without undergoing any change, and it only explodes when heated to a comparatively high temperature.

Ammonium nitride, N_4H_4, obtained as above, is readily purified by adding ether to the alcoholic solution, or it may be crystallised from alcohol, from which it is deposited in plates closely resembling ammonium chloride, but not belonging to the regular system. It is excessively volatile, and explodes violently when heated in a combustion tube with cupric oxide in a current of air; it may, however, be sublimed by cautiously heating at a little above 100°, although violent explosions occur if it is rapidly heated.

Hydrazine nitride, N_5H_5, is prepared by adding hydrazine hydrate to ammonium nitride or to the free acid; it crystallises in long, lustrous prisms, or in plates, and is sparingly soluble in alcohol. By detonation, or on rapidly heating, the compound explodes violently, but it will burn quietly with a smoky, slightly yellow flame; if the combustion takes place on a metallic surface, every trace of oxide on it will be reduced and the metal will appear bright and polished.

The formation of diazohippuramide, $COPh{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}OH$, has already been described; it combines with ammonia, aniline, hydrazine, and similar compounds with elimination of azoimide, whilst the action of water, alcohol, aldehydes, or acidyl hydrazines causes nitrogen to be evolved; for example, the action of aniline on diazohippurylamide gives rise to hippurylanilide, aniline nitride, and water; the reaction with alcohol is represented by the equation,

$$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N_2{\cdot}OH + EtOH = N_2 + NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}OEt + H_2O.$$

On treating diazohippurylamide with benzoylhydrazine, nitrogen and water are eliminated, and a compound is formed which has the formula $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}NHBz$; this is exceedingly stable towards acids and alkalis, and attempts to hydrolyse it have hitherto been unsuccessful; its properties and mode of formation prove it to be a derivative of *triamide*, $NH_2{\cdot}NH{\cdot}NH_2$, which has not as yet been obtained in the free state. J. B. T.

The Colour of Nitric Acid. By L. Marchlewski (*Ber.*, **24**, 271—3276).—It is well known that as water is added to red fuming nitric acid, the colour changes through green to blue and finally disappears. In explanation of this, it has always been assumed that the red acid is a solution of nitrogen peroxide, N_2O_4, in nitric acid, and that the water added decomposes the peroxide with formation of nitric and nitrous acids. The solution of nitrous acid in nitric acid is blue, and this, with the red solution of still undecomposed peroxide, gives a green colour. As more water is added, this excess of peroxide is decomposed, and nothing is then left but a blue solution of nitrous acid.

The author has investigated the matter experimentally in the following manner:—The gases contained in the coloured acid were expelled by means of carbonic anhydride and collected in concentrated sulphuric acid, with which nitrous acid forms nitrosyl hydrogen sulphate,

but with nitrogen peroxide forms a mixture of nitrosyl hydrogen sulphate with nitric acid in molecular proportion. The total nitrogen was determined with the nitrometer, and the reducing power by titration with permanganate. Both results were calculated to trioxide, and from the ratio of the second to the first a conclusion could be drawn as to the constitution of the mixture of gases absorbed. If the gas were pure trioxide, the ratio would of course be 1; if it were pure peroxide, 0·5, since the reducing power of the peroxide is only half that of the trioxide. The results obtained were astonishing, for although they showed that the blue acid contained pure trioxide, yet they also showed that the green acid did not contain more than at most mere traces of the peroxide. The author was consequently led to suspect that his results were vitiated by the presence of nitric oxide, NO, in the coloured acids examined; and in fact when the experiments were repeated, the gases that escaped absorption in the strong sulphuric acid being passed through a strongly acid permanganate solution, the permanganate was perceptibly reduced. The reduction was, of course, due to nitric oxide, and a great deal of this gas must have been present originally, for had only a small quantity been there, it would have formed nitrosyl hydrogen sulphate with the peroxide also present and the concentrated sulphuric acid, and would thus have been absorbed.

The solutions investigated were made by passing the gaseous oxide into pure nitric acid. Solutions obtained by mixing pure liquid peroxide with nitric acid of different strengths are now being investigated. C. F. B.

Boron Phosphoiodides. By H. Moissan (*Compt. rend.*, **113**, 624—627).—Melted phosphorus acts with great energy on boron triiodide, and if red phosphorus is heated in the vapour of the iodide, decomposition takes place with incandescence. If, however, a solution of the iodide in carbon bisulphide is mixed with a similar solution of phosphorus, great care being taken to avoid the presence of moisture, the reaction takes place more slowly. The mixture is sealed up in a flask and kept at the ordinary temperature of the laboratory; it is at first clear, but has a red colour. In a few minutes a brown precipitate begins to separate, and the reaction is complete in about three hours. The product is filtered through glass wool, washed with carbon bisulphide, and dried in a vacuum, the apparatus being filled with carbonic anhydride until the latter is removed by the pump.

The product is *boron phosphodiiodide*, BPI_2, an amorphous, homogeneous, deep-red powder. When heated in a vacuum, it melts at 190—200°, and will remain in superfusion at the ordinary temperature for a long time; in a vacuum, it begins to volatilise at 170—200°, and condenses on the cold part of the tube in distinct red crystals. It is only very slightly soluble in carbon bisulphide, and seems to be completely insoluble in benzene, phosphorus trichloride, and carbon tetrachloride. It is extremely hygroscopic, and decomposes very rapidly in moist air. In presence of a large excess of water, it becomes yellow, without apparent development of heat, and hydriodic, phosphorous, and boric acids are formed, a small quantity of phosphine

being evolved, and a small quantity of a yellow substance with an odour of phosphorus being deposited. With a very small quantity of water, the yellow precipitate is produced in larger quantity, and a distinct quantity of phosphonium iodide is formed.

Boron phosphodiiodide, when heated in hydrogen sulphide, yields boron sulphide, phosphorus sulphide, and hydrogen iodide without any free iodine. Dilute nitric acid yields phosphoric acid and boric acid. whilst strong nitric acid produces the same result, but with incandescence. Sulphuric acid (even Nordhausen) has no action in the cold, but, on heating, free iodine, hydrogen iodide, and sulphurous anhydride are evolved. Phosphorous trichloride and carbon tetrachloride have no action even in sealed tubes at 100°. Chlorine produces incandescence, with formation of boron chloride, iodine chloride, and phosphorus pentachloride. When heated in oxygen, the compound burns and yields iodine, boric anhydride, and phosphoric anhydride. Sodium has no action in the cold, but decomposition takes place at the melting point of the metal. Powdered magnesium reacts with incandescence. When thrown into mercury vapour, the phosphodiiodide takes fire at once. In presence of carbon bisulphide the behaviour of metals is different; magnesium or sodium at the ordinary temperature produces a red compound, PBI, whilst silver or mercury in the cold, or more rapidly at 100°, yields a maroon-coloured compound with the properties of boron phosphide, BP.

Boron phosphoiodide, BPI, is obtained by heating the preceding compound in hydrogen, and is an amorphous, red powder, somewhat less hygroscopic than the diiodide. It volatilises in a vacuum at 210—250° without previous fusion, and condenses in orange-yellow crystals. Strong nitric acid decomposes it with development of heat and without incandescence, iodine being liberated. Concentrated sulphuric acid has no action in the cold, but, on heating, iodine, sulphurous anhydride, and boric acid are formed. When heated out of contact with air, it decomposes at a temperature below dull redness with evolution of vapours of iodine and boron phosphide. Mercury in excess, in presence of dry carbon bisulphide, yields mercuric iodide and boron phosphide at the ordinary temperature.

Boron phosphide, BP, resembles the phosphoiodide BPI in its general properties. It can be obtained by heating the phosphoiodide in hydrogen, and if the heating is continued, a residue of the composition B_5P_3 is left. C. H. B.

Reducing Action of Graphitoïdal Silicon. By H. N. Warren (*Chem. News*, **64**, 75).—When the oxides of easily reducible metals, such as lead, copper, and silver, are heated to dull redness with powdered graphitoïdal silicon, they are reduced to the metal, and if the silicon is in excess, a metallic silicide is formed. The oxides of chromium, tungsten, and molybdenum may also be reduced in this way. In some cases, the reduction takes place with explosive violence; when, for instance, a small quantity of a mixture of equal parts of finely-divided silicon, aluminium, and litharge was melted before the blowpipe, the explosion was so violent as to indent the supporting brick. Jn. W.

Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Solutions of Sodium Chloride. By K. Reich (*Monatsh.*, **12**, 464—473).—The solubility of sodium carbonate at 15° in a solution of sodium chloride of gradually increasing concentration at first diminishes and then increases. The solubility y as a function of the quantity x of sodium chloride in 100 parts of water is expressed by the formula

$$y = 61{\cdot}406 - 2{\cdot}091077x + 0{\cdot}055493x^2 - 0{\cdot}000297357x^3.$$

Accordingly, the minimum lies near $x = 23{\cdot}15$ where $y = 39{\cdot}05$. On passing carbonic anhydride through the saturated solution, the amount of bicarbonate precipitated increases with the quantity of sodium chloride in solution; but a maximum cannot be recognised.

G. T. M.

Allotropic Silver. By M. C. Lea (*Phil. Mag.* [5], **32**, 337—342).—The blue form of allotropic silver is capable of change into an intermediate yellow form which seems to be identical with that into which the gold-coloured form passes under the influence of various causes (Abstr., 1891, 803). The change takes place at about 180°, both with lumps of the blue silver and with films. By the action of sulphuric acid, however, blue silver can be converted into yellow silver at the ordinary temperature, and consequently with retention of all its active properties.

40 grams of sodium hydroxide and 40 grams of yellow or brown dextrin are dissolved in 2000 c.c. of water, and 28 grams of silver nitrate is added in successive very small quantities, with frequent agitation. The solution is slightly turbid, and is deep-green by reflected light, red by transmitted light. The precipitate that forms spontaneously or is produced by the addition of acetic acid, dilute nitric acid, and many neutral substances, consists of blue silver, but if sulphuric acid is added, the precipitate, when dried in films, is blue, green, yellowish-green, or yellow, according to the proportion of acid used. When the silver solution is mixed with an equal volume of a mixture of 7·5 c.c. of sulphuric acid and 92·5 c.c. of water, the precipitate consists wholly of yellow silver, but with higher proportions of acid the product dries with a coppery shade. The lustre of the product diminishes as the proportion of acid used for precipitation is increased.

Conversely, a solution which would yield yellow silver under ordinary circumstances can be made to yield blue silver by the addition of an alkali, and it is immaterial whether the alkali is added to the ferrous tartrate or the silver mixture or to a mixture of the two. There is, therefore, a tendency for acids to produce the yellow product and alkalis the blue product, but it is a tendency only, and both forms can be obtained from neutral solutions; for instance, ferrous tartrate and silver tartrate yield gold-coloured silver, but ferrous citrate and silver citrate produce the blue variety.

When sodium hypophosphite is added to silver nitrate, there is no reduction, but if phosphoric acid is added so that hypophosphorous acid is liberated, a transient red colour appears, and red and blue

stains are formed on the side of the vessel. Phosphorous acid gives similar though somewhat less distinct results.

The blue silver obtained by adding the soda-dextrin silver solution to an equal volume of water containing 4 per cent. of sulphuric acid is not only constant in character but is one of the forms most sensitive to light. When this form is exposed to light, it first becomes more distinctly blue, then yellowish-brown, and finally is converted into the golden-yellow intermediate or crystalline form, with great brilliancy and lustre.

It is noteworthy that the action of light on this blue variety at first increases its sensitiveness to reagents such as potassium ferricyanide, and afterwards reduces it. This is well shown if one part of a film is covered with an opaque substance, another part with a translucent substance, whilst the third is left uncovered, and the three are exposed simultaneously to bright sunlight for about five hours and afterwards treated with dilute ferricyanide solution. The author regards this phenomenon as analogous to the reversing action observed with gelatinobromide plates.

The production of reduced silver is *direct* when an ordinary silver compound is converted into metal without formation of a sub-salt, and *indirect* when the silver compound is first reduced to a sub-salt, and the latter is afterwards reduced to the metal. It would seem that only under the latter conditions is there any formation of allotropic silver. If, in any of the three principal methods of producing allotropic silver, the action is interrupted by the addition of hydrochloric acid, a dark, chestnut-brown or purple-brown mixture of the subchloride with the photochloride is obtained, and from it beautiful rose-red photochloride can be obtained by treatment with cold dilute nitric acid after complete removal of the hydrochloric acid. This result is only obtained by interrupting the reaction before it is complete, and if the hydrochloric acid is added after complete reduction, only grey, normal silver is precipitated. In every case examined, silver subchloride is obtained as one of the products when a reaction resulting in the formation of allotropic silver is interrupted by the addition of hydrochloric acid before reduction is complete.

The rich and varied colour of silver sub-salts would seem to indicate that in these compounds the metal exists in an allotropic form, but, on the other hand, the greater activity of allotropic silver and its lower sp. gr. would tend to show that the allotropic form has a simpler molecular structure than the normal metal. C. H. B.

Colloïdal Silver. By E. A. Schneider (*Ber.*, **24**, 3370—3373).—Colloïdal silver prepared according to Carey Lea's method, by the reduction of silver nitrate with ferrous citrate, cannot be purified by dialysis alone; the better plan is to separate the solid colloïd from the mother liquor as completely as possible by filtration, then to dissolve the silver in a little water and allow this solution to dialyse. On adding hydrochloric acid to aqueous colloïdal silver solutions, silver and argentic chloride are precipitated, the proportion of the latter being greater with increasing quantities of hydrochloric acid; the mixed precipitate is extracted with ammonia, the argentic chloride

precipitated by acidification with nitric acid, and hydrochloric acid added to the filtrate; if the quantity of hydrochloric acid originally employed was small, a further precipitate is produced, showing the presence of a silver subchloride. The mixed precipitate of silver and argentic chloride was always rose-red.

Nitric and sulphuric acids react with colloïdal silver solutions in a similar manner. No evolution of hydrogen could be detected even when sufficient hydrochloric acid was added to the silver solution to produce a considerable precipitate of argentic chloride; this may indicate the presence of argentous oxide: neither was oxygen evolved when, in consequence of the small quantity of hydrochloric acid employed, the precipitate consisted of almost pure silver.

J. B. T.

Direct Combination of Chlorine and Bromine with Metals. By H. Gautier and G. Charpy (*Compt. rend.*, **113**, 597—600).—Well cleaned wires of various metals, 2 mm. in diameter, were kept in the dark in contact with dry bromine for a definite length of time at 15° and 100°. The percentage loss of weight in each case is given in the following table:—

	At 15° in 8 days.	At 15° in 4 months.	At 100° in 8 days.
Magnesium	0·0	0·0	0·19
Zinc	0·289	0·487	0·63
Iron	0·210	0·440	23·27
Copper	0·371	1·740	6·62
Silver	0·003	0·540	—

Aluminium under similar conditions combines energetically with bromine and becomes incandescent, a burning fragment running about on the surface of the bromine like potassium on water. With liquid chlorine in sealed tubes at the ordinary temperature, the results are similar, the percentage losses being: magnesium, 0·0; zinc, 0·0; iron, 0·740; copper, 3·241; silver, 0·673. Potassium, sodium, and aluminium seem to be unaffected by liquid chlorine at its boiling point, but at −20° aluminium combines with the halogen with incandescence.

In presence of water, the results are very different. Magnesium and aluminium, when placed in bromine-water, produce a regular evolution of hydrogen, and, after some time, an oxybromide separates, the reactions being analogous to the decomposition of water by iodine in presence of aluminium. With zinc, iron, and copper, there is no evolution of gas, and a wire 2 mm. in diameter and 50 mm. in length disappears in seven to eight hours in excess of bromine-water. It seems probable that in these cases the decomposition of water by the halogen is accelerated by the presence of the metal, the latter being converted into an oxide which is attacked by the hydracid formed.

C. H. B.

Lithium Copper Chloride. By A. Chassevant (*Compt. rend.*, **113**, 646—648).—When a concentrated solution of lithium chloride is

added to a concentrated solution of an equivalent quantity of cupric chloride, a magma of crystals of the latter salt is formed, but if the mixture is evaporated in a vacuum over phosphoric acid or on a water-bath at 100°, the crystals dissolve, the liquid acquires a brownish-red colour and deposits transparent, garnet-red crystals of the double chloride $2CuCl_2,2LiCl,5H_2O$. When exposed to the air, they decompose, and become opaque, crystals of cupric chloride separating, whilst the lithium chloride deliquesces. If heated rapidly to 130°, they melt in their water of crystallisation and form a deep-brown, almost black, solution. At a higher temperature, the salt, like lithium chloride under similar conditions, decomposes and evolves chlorine. When heated slowly in an oven, or in a current of dry air, the crystals become anhydrous at 100—120°, but some hydrochloric acid is likewise given off, and, on treatment with water, a residue of cupric oxychloride is left. The double salt can be obtained as an anhydrous, chamois-coloured powder by heating it at 120° in a current of dry air mixed with dry hydrogen chloride. It is decomposed by water, but can be recrystallised from a concentrated solution of lithium chloride. C. H. B.

Formation of Saline Hydrates at High Temperatures. By G. Rousseau (*Compt. rend.*, **113**, 643—646).—When the hydrated sodium ferrite obtained at 800°, and previously described, is allowed to remain in contact with glycerol for several days, and is washed first with this liquid and afterwards with absolute alcohol, the dried residue contains only 9·68 per cent. of water, instead of the 14·5 per cent. that it contains when water is used for washing. The ferrite, $14Fe_2O_3,13H_2O,Na_2O$, when treated with glycerol in a similar manner, loses 2·79 per cent. of water. If either of these compounds is heated at 100° with glycerol, its colour rapidly becomes darker, and if digestion is prolonged, the whole of the water and alkali is removed, and anhydrous ferric oxide remains.

The sodium manganites, such as $12MnO_2,4H_2O,Na_2O$, are not affected in a similar way by glycerol.

The author considers that these results establish his previous conclusions and support the view that the alkaline oxide replaces part of the water. C. H. B.

Crystallised Ferric Oxychlorides. By G. Rousseau (*Compt. rend.*, **113**, 542—544).—Very concentrated solutions of ferric chloride, containing about 80 per cent. of Fe_2Cl_6, maintained at a temperature of 160—220° for some time, yield a crystallised ferric oxychloride, $2Fe_2O_3,Fe_2Cl_6 + 3H_2O$. By prolonged boiling with water, this compound is gradually converted into a ferric hydroxide, $(Fe_2O_3 + H_2O)_3$, which retains the same crystalline form as the oxychloride.

Solutions containing 85 to 90 per cent. of the anhydrous ferric chloride have been heated in sealed tubes, together with a fragment of marble or giobertite. Between 225° and 280°, red-brown lamellæ of the oxychloride $2Fe_2O_3,Fe_2Cl_6$ are obtained. Between 300° and 340°, large plates of a brownish-black oxychloride $3Fe_2O_3,Fe_2Cl_6$ are formed.

The author has been unable to study the reaction at higher temperatures, but believes that a series of oxychlorides of the type $(Fe_2O_3)_n,Fe_2Cl_6$ would be formed, in which the proportion of Fe_2O_3 would increase with the temperature.

The anhydrous oxychlorides are very sparingly soluble in dilute mineral acids. When boiled with water in presence of marble for 150—200 hours, they lose all their chlorine as hydrochloric acid, ferric oxide of a fine brownish-red colour remaining.

The optical properties of these oxychlorides have been determined by Fouqué. They occur in prisms giving longitudinal extinction. The plane of their optic axes is transverse, and the bisectrix is positive.

It would be interesting to observe whether the rhombic oxychlorides retain their form during the concentration of ferric oxide in the molecule, or whether they assume, at a temperature near a red heat, the hexagonal form characteristic of ferric oxide. On the latter hypothesis, the hydrolysis of the hexagonal oxychloride, by boiling with water, should give a new method for the synthesis of hæmatite, allowing the determination of the degree of polymerisation of this mineral oxide. W. T.

Action of Water on Glass. By E. Pfeiffer (*Ann. Phys. Chem.* [2], **44**, 239—264).—The author has taken advantage of electrolytic conductivity for the purpose of determining the amount of substance dissolved from glass by water at low temperatures. Ordinary chemical methods give very uncertain numerical results, on account of the difficulty in determining the exact magnitude of the large surface which must be exposed to the action of water, and even these results are obtained under conditions diverging considerably from those of laboratory practice.

Water first of all dissolves practically pure alkali (potassium or sodium hydroxide) out of the glass, and this afterwards exerts its own influence by dissolving silica. The author estimates the amount of alkali dissolved by determining the electrical conductivity of the solution, to which it is proportional. As the molecular conductivities of potassium hydroxide and sodium hydroxide lie close together (220×10^{-7} and 200×10^{-7}, according to Kohlrausch), no great error is committed in estimating the total amount dissolved on the assumption that each alkali dissolves proportionately to the extent to which it is contained in the glass. When silicates are formed in the solution, the conductivity falls.

The experiments were made by exposing cylinders of good Thuringian glass with known surface to the action of water contained in glazed porcelain vessels; the temperature in the three series of observations made being 10°, 20°, and 30°. For one sort of glass at a given temperature, it was found that $\Delta_0 = \Delta w/o$ is a constant, Δ being the increase in conductivity per hour, w the volume of water, and o the surface of the cylinder. When the glass has been exposed for some time to the action of water at a temperature of 60°, the value of Δ_0 for 20° falls considerably. $\Delta_0^{(20)}$ for the first day is much

greater than $\Delta_0^{(20)}$ afterwards. With the specimen of glass examined, it was found that at 20° one to two millionths of a milligram were dissolved out by 1 c.c. of water per square centimeter in an hour. No silica is dissolved at 10° or 20°. At 30°, however, a considerable falling off of Δ_0 with the time is observed, due in all probability to this cause. The values of Δ_0 (reduced to 20°) for the various temperatures are as follows:—

	10°.	20°.	30°.
Δ_0.....	25	100	673

Prolonged treatment of the glass at a low temperature does not appreciably affect its solubility at a higher temperature. J. W.

Stannibromides. By Leteur (*Compt. rend.*, **113**, 540—542).—The stannibromides of the alkali metals and magnesium are yellow, well-crystallised substances. Concentrated solutions have the same colour, but at a certain state of dilution, the colour disappears. The anhydrous stannibromides of potassium and ammonium only suffer change in very moist air; others are very deliquescent. Concentrated solutions may be heated without decomposition; on dilution, decomposition occurs with the formation of hydrobromic acid and the deposition of hydrated tin dioxide. Alcohol decomposes these compounds, slowly in the cold, more rapidly on heating; benzene has no action on them.

The general method for the preparation of the stannibromides consists in mixing concentrated solutions of the two bromides and evaporating the mixture in a vacuum or in dry air.

The ammonium salt, $(NH_4)_2SnBr_6$, forms sulphur-yellow octahedra belonging to the cubic system; it decrepitates when heated, and volatilises with partial decomposition.

The sodium salt, $Na_2SnBr_6 + 6H_2O$, forms yellow prisms of the monoclinic system, having a position of extinction in polarised light at 15° to the longer axis. It is very deliquescent, but effloresces rapidly over sulphuric acid or in a vacuum. It decomposes, when heated, with evolution of water and stannic bromide.

The lithium salt is probably $Li_2SnBr_6 + 6H_2O$, but the water cannot be accurately determined owing to the extreme deliquescence of the compound. It forms small, yellow, prismatic needles which act on polarised light, and appear to belong to the monoclinic system. Over sulphuric acid, these crystals effloresce, giving a citron-yellow, crystalline powder tending towards the composition $Li_2SnBr_6 + 5H_2O$.

The magnesium salt, $MgSnBr_6 + 10H_2O$, gives small, sulphur-yellow, monoclinic crystals. The ordinary form is a prism showing the faces g_1 and h_1 with modifications on the angle a. Macles are frequent. Extinction occurs at an angle of 60°.

The study of the alkaline earthy stannibromides is being now carried on. W. T.

Dissolution of Bismuth Chloride in a Saturated Solution of Sodium Chloride: Basic Bismuth Salicylate. By H. Causse (*Compt. rend.*, **113**, 547—549).—Sodium chloride, like ammonium chloride, may be employed instead of free acid to prevent the dissociation of bismuth salts by water. Hence, in presence of sodium chloride, hydrochloric acid may be completely neutralised by bismuth carbonate or oxide. 100 c.c. of hydrochloric acid solution containing 3·0775 grams HCl is left in contact with 3 grams of bismuth oxide until no further solution takes place; the remaining oxide is collected and weighed. 1·50 grams of the oxide are dissolved, requiring 0·4775 gram of the acid to form $BiCl_3$; the remaining 2·60 grams of the hydrochloric acid are required to maintain the equilibrium in the solution.

With 100 c.c. of acid containing 6·155 grams HCl, 6·00 grams of oxide are dissolved, and 3·117 grams of free acid remain. With 100 c.c. of acid containing 9·2325 grams HCl, 10 grams of oxide are dissolved, and 4·557 grams of acid remain. Each of these solutions is saturated with common salt, and then treated with bismuth oxide. The quantities of bismuth oxide dissolved as compared with the quantities required to neutralise the hydrochloric acid present with production of bismuth trichloride are respectively 6·80 : 6·584, 13·25 : 13·160, and 20·25 : 19·70.

The numbers given above do not show that any definite relation exists between the free acid and the amount of bismuth chloride formed. To ascertain whether such a relation exists at the experimental limit, the author treats 50 grams of oxide with 50 c.c. of saturated hydrochloric acid containing 22·80 grams of acid. 47·50 grams of oxide are dissolved, and 5·18 grams of free acid remain. 5·40 grams of acid would be uncombined if the reaction were as follows: $Bi_2O_3 + 8HCl = 2(BiCl_3,HCl) + 3H_2O$; hence the author concludes that under these circumstances a definite salt is formed.

To obtain basic bismuth salicylate, 40 c.c. of concentrated hydrochloric acid is saturated with bismuth oxide in presence of 500 c.c. of saturated sodium chloride solution; to another 500 c.c. of brine are added 9 grams of soda and 22 grams of sodium salicylate, the two solutions are mixed, and the precipitate formed is washed with water containing a few drops of nitric acid. The basic salicylate, $C_7H_5BiO_4,H_2O$, obtained, forms microscopic prisms, and has properties similar to those of the normal salicylate previously described. It is decomposed by heat with loss of the whole of its salicylic acid, which may also be completely eliminated by boiling concentrated alcohol. The constitution of this salt may be represented by the formula $OH\cdot C_6H_4\cdot COO\cdot Bi(OH)_2$, which accounts for its ready hydrolysis. W. T.

Mineralogical Chemistry.

Boléite, a New Mineral. By Mallard and E. Cumenge (*Compt. rend.*, **113**, 519—524).—This mineral occurs in cubical crystals of a fine indigo-blue colour in an argillaceous matrix, termed *jaboncillo*, next above the true copper-bearing bed of Boleo, near Santa Rosalia, Lower California. The crystals are accompanied by anglesite, phosgenite, cerussite, and atacamite. They are not decomposed by water; they melt in a candle flame, and, when heated in a closed tube, decompose with evolution of water.

Two analyses of clean samples yield the numbers :—

	I.	II.	Calculated.
Silver	8·85	8·70	8·50
Copper	13·95	14·50	15·00
Lead	48·45	49·75	48·90
Chlorine	19·98	19·00	19·55
Water	4·77	4·00	4·28
Oxygen (by diff.)	4·00	4·05	3·77

The calculated percentages correspond with the formula $3[PbCl\cdot OH,CuCl\cdot OH] + AgCl$. Metallic copper is obtained by reduction in a current of dry hydrogen without the liberation of hydrochloric acid; this would seem to indicate that the chlorine is not combined with the copper, but, in reality, the hydrochloric acid formed immediately reacts on the lead oxychloride, producing lead chloride and water. The formula given best shows the relationships of this mineral to laurionite, $PbCl\cdot OH$, and atacamite,

$$CuCl\cdot OH,Cu(OH)_2.$$

Brooke's percylite, from Sonora, may possibly be the same mineral, although its imperfect analyses do not indicate the presence of silver.

In hardness, the mineral is a little superior to calcite, and its density is 5·08. The common form is the cube without modifying faces. Some crystals show very sharp and brilliant octahedral faces; more rarely, dodecahedral faces are met with. Some small crystals have been observed with the edges replaced by re-entering angles formed by faces of the hexakistetrahedron. The cleavage is distinct and easy, parallel to the faces of the cube, the octahedral cleavage being less distinct. The observed optical properties are those of very birefringent, negative, uniaxial crystals; the index of refraction could not be accurately determined; for a prism formed by the cubical and dodecahedral faces, its approximate value is 2·07. Boléite belongs to the tetragonal system, though pseudo-cubic in habit.

Along with the cubical crystals, octahedral crystals occur in peculiar groupings, showing the octahedral faces brilliant, but generally formed of three facettes, composing a low pyramid.

The angular measurements are difficult, and only yield approximately the values for the parameters, $a : c = 1 : 1{\cdot}645$. The composition of the octahedral crystals is the same as that of the cubical crystals:—

	Cubic cryst.	Octahedral cryst.	Calculated.
Silver.....	9·2	9·4	8·5
Copper.....	14·8	15·0	15·0
Lead.....	50·2	50·7	48·9
Chlorine.....	19·4	19·7	19·5

Their densities appear to be about the same, a small specimen of the octahedral crystals giving 5·0. W. T.

Polydymite, Ullmannite, and Wolfsbergite. By H. Laspeyres (*Zeit. Kryst. Min.*, **19**, 417—436).—1. *Polydymite.*—The author brings forward fresh evidence in support of the formula Ni_4S_5 he propounded 15 years ago for polydymite and nickel-bismuth glance, minerals which he regards as identical. The accuracy of this formula is confirmed by the analysis of the polydymite from Sudbury, in Canada, as well as by the examination of some excellent crystals of this mineral from the Grüneau mine, in the Siegen district.

2. *Ullmannite.*—The author describes some crystals of ullmannite, from the Landeskrone mine, near Siegen. Although this mineral is of frequent occurrence in the Siegen mines, it has never before been found in crystals.

3. *Wolfsbergite.*—Of the crystalline form of the copper-antimony glance (Wolfsbergite), from Wolfsberg, in the Harz, all that is known is the brief account given by G. Rose in 1835. A discovery of a well-crystallised specimen in the Bonn Museum has enabled the author to give a detailed description of the crystallography of this mineral. The forms he has observed are:—0P, $\frac{3}{7}\bar{P}\infty$, $\bar{P}\infty$, $2\bar{P}\infty$, $\breve{P}\infty$, $\frac{7}{4}\breve{P}2$, $\frac{8}{3}\bar{P}\frac{4}{3}$, $\frac{7}{9}\breve{P}3$. The axial ratio is $a : b : c = 0{\cdot}52830 : 1 : 1{\cdot}62339$. B. H. B.

Some New Chilian Minerals: Darapskite, Lautarite, Iodochromate. By A. Dietze (*Zeit. Kryst. Min.*, **19**, 445—451).—1. *Darapskite.*—This is the name given by the author to a new double salt of the composition represented by the formula $NaNO_3 + Na_2SO_4 + H_2O$. It is colourless, transparent, and occurs in square tablets bevelled by tetragonal pyramids. The new mineral is found at the Pampa del Toro, and is named after Dr. L. Darapsky, the well-known mineralogist, of Santiago.

2. *Lautarite.*—Although it has long been known that the iodine contained in the *caliche* or raw nitrate is due to the presence of iodates, no iodate has hitherto been found as a distinct mineral species. The new mineral described by the author is calcium iodate, the analytical results being in accord with the formula $Ca(IO_3)_2$. It occurs at the "Pampa del Pique III," in the form of large, monoclinic prisms, having the sp. gr. of 4·59. It is transparent, and of a yellowish colour. It is very slightly soluble in water.

3. *Iodochromate.*—Near the chief locality of lauterite, small, yellow

crystals occur in the caliche. These prove on analysis to be a double iodate and chromate of calcium, of the formula $7Ca(IO_3)_2,8CaCrO_4$. The accuracy of this formula is shown by the results of seven analyses. B. H. B.

Formula of Axinite. By A. Kenngott (*Jahrb. f. Min.*, 1891, ii, Mem. 335—336).—In a recent paper (Abstr., 1891, 1168), the author published a formula for axinite calculated from two analyses given by Whitefield. This result he now compares with three analyses given by F. A. Genth (*Amer. J. Sci.*, **41**, 394). These analyses refer to axinite from Franklin, New Jersey, in crystals and in lamellæ, and from Guadalcazar, in Mexico. The analyses of axinite from Franklin give results closely approaching those obtained from Whitefield's analyses. The axinite from Guadalcazar, however, was apparently admixed with white felspar partially converted into kaolin, and, consequently, cannot be considered sufficiently pure to serve as the basis for the calculation of a formula. B. H. B.

Constitution of certain Micas, Vermiculites, and Chlorites. By F. W. Clarke and E. A. Schneider (*Amer. J. Sci.*, **42**, 242—251).—In a previous paper (Abstr., 1891, 529), the authors considered the constitution of the mica and chlorite groups. The present paper is a continuation of the same research. Throughout the investigation the fundamental hypothesis that the minerals studied are substitution derivatives of normal salts has been amply justified.

Of the so-called vermiculites, two only, jefferisite and kerrite, were considered in the former paper, and these were shown to be trihydrated micas in which the original alkalis had been replaced by hydrogen. The examination of other varieties shows that kerrite is essentially a trihydrated hydrophlogopite. Protovermiculite, from Magnet Cove, Arkansas, is the same substance mixed with an equal proportion of trihydrated hydroclintonite. Jefferisite is a similar mixture of hydrobiotite and hydroclintonite, also trihydrated. An altered biotite, from Henderson Co., North Carolina, is found to be essentially a biotite, about half way changed into a vermiculite, and is interesting as a transition product. All the vermiculites are not so simple as the above-named minerals. In some members of the group, there seems to be a small admixture of chloritic molecules, and it is even probable that many intermediate stages between mica and chlorite may exist. As bearing on this question, the authors give analyses of the hallite from Nottingham, Chester Co., Pennsylvania, and of the vermiculites from Lennie, Delaware Co., Pennsylvania. They also give the results of their examination of vermiculites from Newlin, Chester Co., and from Middletown, Delaware Co., in both of which Tschermak's view, that some of the vermiculites are probably chlorites, is partly sustained. A very interesting example of the way in which the chloritic vermiculites approach the serpentines in composition has been furnished by a specimen found at Old Wolf Quarry, Chestnut Hill, Easton, Pennsylvania, an analysis of which is given by the authors. Lastly, there is one other mineral examined during this investigation, a pale, yellowish-green mica, from

Auburn, Maine, where it occurs in direct contact with ordinary muscovite. Analysis shows that it has the composition of muscovite. The case is interesting as showing a secondary growth of muscovite on muscovite, with a marked difference in outward appearance between the two formations. B. H. B.

Genesis of Iron Ores by Replacement of Limestone. By J. P. Kimball (*Amer. J. Sci.*, **42**, 231—241).—The object of this memoir is to show that the well-recognised products of epigenesis, like siderite and ferrocalcite, are, as a rule, also products of direct pseudomorphous replacement of isomorphous calcium carbonate. From this it follows that secondary or indirect replacement of calcium carbonate by ferric hydroxide is wrought through alteration of pseudomorphous siderite or ferrocalcite, and also, through progressive alteration, by ferric oxide and even by magnetic oxide. As the result of his investigations, the author advances the proposition that deposits of concentrated iron ores occur far more extensively as pseudomorphous replacements than has hitherto been made to appear, and far more extensively than by original sedimentation of ferric hydroxide. B. H. B.

The Basalt of the Stempel, near Marburg. By M. Bauer (*Jahrb. f. Min.*, 1891, ii, Mem. 231—271).—This is the concluding instalment of an elaborate monograph (compare Abstr., 1891, 1440) on the basalt occurring at the hill known as the Stempel, which rises above the sandstone of the Lahn plateau. This section deals with the inclusions met with in the rock. These inclusions consist of limestone, quartz, apatite, nepheline, felspar, amphibolite, titanite, and zircon. B. H. B.

Organic Chemistry.

Preparation of Bromoform from Acetone and Sodium Hypobromite. By G. Denigès (*J. Pharm.* [5], **24**, 243—247).—A litre flask is charged with 100 c.c. of soda lye, 200 c.c. of water, and then 20 c.c. of bromine. After gentle shaking from time to time, the liquid becomes uniformly yellow, when sufficient acetone (about 10 c.c.) is added to decolorise the solution. There is quickly formed an almost colourless layer of bromoform. The product is washed repeatedly with water, from which it can be easily separated by filtration, and the compound is usually pure enough for immediate employment. The reaction takes place in two stages: sodium hypobromite and sodium bromide are first formed; then the hypobromite and acetone react, forming bromoform, sodium acetate, and sodium hydroxide. The yield is 60—70 per cent. of that theoretically possible. The bromoform should be removed from contact with hypobromite as soon as possible, otherwise carbon tetrabromide is

produced. A pure sample of bromoform boiling at 150 (768 mm.) had a density of 2·906 at 12° and 2·897 at 18°, or say 2·90 at about 15°, confirming Cahours' previous determination of 2·90 at 12°.

J. T.

Monobromobutylenes. By E. Reboul (*Compt. rend.*, **113**, 589—592).—When the bromide $CHMeBr{\cdot}CHMeBr$, boiling at 150°, and obtained by the action of bromine on symmetrical dimethylene, $CHMe{:}CHMe$, is treated with alcoholic potash, it yields a mixture of the two bromobutylenes, $CHMe{:}CMeBr$ and $CHMeBr{\cdot}CH{:}CH_2$.

A new brombutylene, $CH_2Me{\cdot}CBr{:}CH_2$, is obtained by the removal of HBr from ethylethylene bromide. Normal bromobutane is mixed with one-third the theoretical quantity of bromine, together with water, and the mixture exposed to sunlight in a small, closed flask until it is colourless. The product is then distilled, and the fraction boiling below 160° is treated again with bromine in a similar manner. The successive products boiling above 160° are mixed and fractionated, when they yield ethylethylene bromide boiling at 166° and free from isomerides.

When ethylethylene bromide is treated with alcoholic potash in the ordinary manner, it yields monobromobutylene boiling at 88° under a pressure of 759 mm.; it is a colourless liquid with an alliaceous odour; sp. gr. 1·282 at 21°. Since the boiling point is 3° below that of Boutlerow's bromisobutylene, $CMe_2{:}CHBr$, it is almost certain that it has the bromine at the end of the chain that is removed from the ethylethylene bromide. If the compound is heated at 100° in a sealed tube with alcoholic potash, it yields a light, mobile liquid which has a strong alliaceous odour, and boils at 14—14·5° under a pressure of 761 mm. With ammoniacal cuprous chloride, it forms a deep sulphur-yellow compound, and with ammoniacal silver nitrate, a white compound, both of which yield the hydrocarbon when treated with dilute acids. The hydrocarbon is probably identical with the ethylacetylene obtained by Bruylants from methyl ethyl ketone chloride.

In view of this decomposition, the monobromobutylene may be called ethylacetylene α-hydrobromide. It combines with bromine with great energy, yielding a tribromobutane, $CH_2Me{\cdot}CBr_2{\cdot}CH_2Br$, which boils at 112—115° under a pressure of 40 mm. and with partial decomposition at 214—218° under the ordinary pressure; it is a colourless liquid of sp. gr. 2·136 at 17°. It is not identical with the product of the action of bromine on normal butyl bromide in presence of sunlight; the latter boils at 117—122° under 40 mm., and its sp. gr. at 17° is 2·171.

Ethylacetylene α-hydrobromide combines slowly with aqueous hydrobromic acid in the cold, but more rapidly at 100°, yielding a mixture of the bromide boiling at 166° and a lower bromide, probably $CH_2Me{\cdot}CMeBr_2$. Boutlerow's bromisobutylene behaves differently under similar conditions.

C. H. B.

Penterythritol: a Tetrahydric Alcohol obtained from Formaldehyde and Acetaldehyde. By B. Tollens and P. Wigand (*Annalen*, **265**, 316—340).—A crystalline compound, which the

authors name penterythritol, is formed, together with volatile fatty acids, amorphous, syrupy substances, aldehydes, and small quantities of a crystalline substance, the nature of which has not yet been determined, when a mixture of formaldehyde (194 grams), acetaldehyde (60 grams), water (9 litres), and calcium hydroxide (160 grams) is kept for one to two months, or longer, at the ordinary temperature with frequent shaking. The boiling, filtered solution is treated with a quantity of oxalic acid exactly sufficient to precipitate the calcium in solution, then filtered, and evaporated to a syrup; on keeping for some time, the residue solidifies to a mass of yellowish crystals, and is purified by recrystallisation from water with the addition of animal charcoal. The yield of the crude, crystalline product, dried on porous earthenware, is about 115 grams.

Penterythritol, $C_5H_8(OH)_4$, crystallises from hot water in large well-defined prisms, melts at 250—255°, and is soluble in about 18 parts of water at 15°; its molecular weight was determined in glacial acetic acid solution with results in accordance with the molecular formula ascribed to it above. Its aqueous solution is optically inactive, even in presence of borax; when a neutral aqueous solution of penterythritol is added to a small quantity of a solution of borax, the latter acquires a distinctly acid reaction. When penterythritol is heated quickly, it gives off an odour recalling that of decomposing glycerol; it does not give the iodoform reaction. The *tetracetyl* derivative, $C_5H_8(OAc)_4$, prepared by heating the alcohol with acetic anhydride and sodium acetate, is a crystalline substance melting at 84°; molecular weight determinations in acetic acid solution gave results agreeing with those required by a compound of the molecular formula given above.

The di-iodhydrin, $C_5H_8I_2(OH)_2$, is formed when penterythritol is heated with concentrated hydriodic acid and amorphous phosphorus at 170—180°; it forms colourless crystals, melts at 130°, and is readily soluble in alcohol, but only sparingly in water. The tri-iodhydrin, $C_5H_8I_3{\cdot}OH$, is produced, together with the tetriodide described below, when penterythritol is heated with concentrated hydriodic acid and amorphous phosphorus at 190° in sealed tubes; when the product is boiled with water, the residue dissolved in alcohol, and the cold solution evaporated, large, rhombic plates melting at 70° are deposited; if these crystals of the tri-iodhydrin are dissolved in hot alcohol, and the solution then allowed to cool, the compound is obtained in lustrous needles melting at 62°. The *tetriodide*, $C_5H_8I_4$, is isolated by extracting that portion of the product which is insoluble in alcohol with boiling benzene, from which it is deposited on cooling in colourless plates melting at 225°.

When penterythritol is oxidised with nitric acid, it gives oxalic acid and an amorphous product the nature of which has not been determined; when treated with chromic acid, it yields formic acid and carbonic anhydride. The constitution of the alcohol is most probably expressed by the formula $C(CH_2{\cdot}OH)_4$. F. S. K.

A Sugar from Quince-juice. By R. W. Bauer (*Landw. Versuchs-Stat.*, 469—470).—When quince-juice is boiled with 5 per cent

sulphuric acid, it yields a sweet syrup which has approximately the same rotatory power as dextrose, and from which a yellow osazone melting at 204° can be obtained. F. S. K.

Cellulose Gum. By W. Hoffmeister (*Landw. Versuchs-Stat.*, **39**, 461—468; compare Abstr., 1890, 581).—When cellulose, prepared in the usual manner, by extracting certain vegetable products with ether, alcohol, water, and cold dilute ammonia successively, is treated with 5 per cent. soda, a considerable, but variable, quantity of wood gum passes into solution; this gum is completely soluble in an ammoniacal solution of copper oxide, and is not destroyed by the "chlorine mixture" previously referred to. If, after extracting with soda, the cellulose is dissolved in an ammoniacal solution of copper oxide, and reprecipitated with hydrochloric acid in the cold, or if it is treated with the chlorine mixture, glacial acetic acid, or dilute ammonia, to free it from incrusting substances, it again yields a considerable quantity of soluble carbohydrates on extraction with 5 per cent. soda; when the portion insoluble in soda is again treated with any of the above-named reagents, a further quantity is rendered soluble, and, by repeating the treatment many times, the whole of the cellulose is obtained in a form which is soluble in 5 per cent. soda.

The quantity which is rendered soluble by any single treatment depends on the source of the cellulose; it would seem, therefore, that cellulose is not a homogeneous substance. For the soluble product obtained in the manner described, Tollens proposes the name cellulose gum; this substance also exists in various forms. F. S. K.

Constitution of the Ligno-celluloses. By C. F. Cross and E. J. Bevan (*Chem. News*, **64**, 63—64).—Cold, dilute, aqueous chromic acid forms a compound with the substance of jute fibre, which by treatment with mineral acids is converted into a brittle, soft substance, lustrous and greenish in appearance, containing from 2 to 2·5 per cent. of chromic oxide, and convertible into an oxycellulose, the alkaline solution of which reduces Fehling's solution on boiling. The yield of the chromium compound from a fibre which gave 74 per cent. of cellulose by the chlorination method was 85—90 per cent., so that a portion of the jute convertible into soluble derivatives by chlorination, here appears to yield products more intimately connected with cellulose. The soluble products of the oxidation are brown, gummy substances, which, when chlorinated, yield substitution products having characteristic colour reactions. The formation of the chromium compound may be regarded as a step in the process of lignification.

The authors draw attention to the substance which Lindsey and Tollens (*Inaug. Diss., Göttingen*, 1891) have isolated from the gummy residue left on evaporation of the waste liquors from the Mitscherlich (bisulphite) fir-wood paper-pulp process; it has the composition

$$C_{24}H_{24}Me_2SO_{12},$$

and appears to be related to the ketonic substance, lignone, previously obtained from jute (Trans., 1889, **55**, 213). Jn. W.

Thio-derivatives of Ethylamine. By S. Gabriel (*Ber.*, **24**, 3098—3104; compare Abstr., 1891, 815).—The action of various substances on ethylmercaptophthalimide, $C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}SH$, has been studied.

A warm solution of ethylmercaptophthalimide (11 grams) in absolute alcohol (25 c.c.) is treated with sodium ethoxide (2·3 grams of sodium in 25 c.c. of alcohol) and bromethylphthalimide (14 grams), and boiled for half an hour in a reflux apparatus. The solution is cooled, and the crystals washed with alcohol and hot water; *diphthalimidoethyl sulphide*, $(C_8H_4O_2{:}N{\cdot}C_2H_4)_2S$, melting at 128—129°, is thus obtained, the yield being two-thirds of the theoretical.

When a solution of ethylmercaptophthalimide (20 grams) in alcohol (50 c.c.) is gradually heated with sodium ethoxide (2·3 grams of sodium in 50 c.c. of alcohol) and then with ethylene chlorhydrin (10 grams), boiled for half an hour in a reflux apparatus, the alcohol driven off, and the residue treated with water, a colourless syrup (20 grams), which will not crystallise, separates; it is doubtless *β-hydroxy-β-phthalimidoethyl sulphide*, $OH{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2$. When warmed with double the volume of phosphorus oxychloride, it yields *β-chloro-β-phthalimidoethyl sulphide*, $C_2H_4Cl{\cdot}S{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2$, which separates out when the mass is poured into water as an oil that gradually crystallises. Recrystallised from acetic acid and alcohol, it forms colourless needles, melts at 76—77°, and dissolves easily in ether, benzene, carbon bisulphide, chloroform, and boiling light petroleum. *β-Bromo-β-phthalimidoethyl sulphide*,

$$C_2H_4Br{\cdot}S{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2,$$

is obtained in a similar manner by using the pentabromide, instead of the oxychloride, of phosphorus. It crystallises from hot light petroleum in long needles, melts at 89—90°, and dissolves readily in ethyl acetate, warm carbon bisulphide, and ethyl and methyl alcohol.

The oxidation of diphthalimidoethyl sulphide has also been studied. When a slight excess of bromine water is added to a solution of the sulphide (3 grams) in hot acetic acid (15 c.c.), *diphthalimidoethyl sulphoxide*, $(C_8H_4O_2{:}N{\cdot}C_2H_4)_2SO$, is formed, and separates, when the solution is cooled, in long needles melting at 191°. When this substance (18 grams) is boiled with 20 per cent. hydrochloric acid (250 c.c.) for three hours in a reflux apparatus, a complex decomposition takes place, resulting in the formation of diamidoethyl sulphoxide, taurine, ammonia, and thioethylamine; for details as to the separation of these, reference must be made to the original paper. *Diamidoethyl sulphoxide picrate*, $SO(C_2H_4{\cdot}NH_2)_2,2C_6H_3N_3O_7$, forms a yellow, crystalline powder which softens at 190°, and melts with decomposition at 200°. *Thioethylamine picrate*, $S(C_2H_4{\cdot}NH_2)_2,2C_6H_3N_3O_7$, forms long, broad prisms softening at 190°, and melting with decomposition at 213°. The *platinochloride*, $S(C_2H_4{\cdot}NH_2)_2,H_2PtCl_6$, forms orange-yellow needles. The *benzoyl* derivative, $S(C_2H_4{\cdot}NHBz)_2$, crystallises from ethyl acetate in scales which soften at 106° and melt at 109—110°.

When diphthalimidoethyl sulphide (6 grams) is dissolved in a

mixture of acetic acid (60 c.c.) and water (6 c.c.) on the water-bath, and chromic acid (5 grams) added, transparent, colourless crystals of *diphthalimidoethylsulphone*, $SO_2(C_2H_4{\cdot}N{:}C_8H_4O_2)_2$, separate (6 grams). This softens at 250°, melts at 255—256° and dissolves very sparingly in most solvents, slightly in hot acetic acid, and can be crystallised from hot nitrobenzene. The same compound may be obtained, although less conveniently, by oxidising an acetic acid solution of the sulphide with potassium permanganate. When the sulphone (3 grams) is heated with alcohol (20 c.c.) and 33 per cent. aqueous potash (3 c.c.), it dissolves, and *ethylsulphonediphthalamic acid* crystallises out when the solution is diluted with water, acidified with hydrochloric acid, and cooled. It forms broad, colourless needles, readily soluble in ammonia and boiling water. The *silver salt*, $SO_2(C_2H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOAg)_2$, forms an amorphous precipitate which changes to a crystalline powder. When the acid is boiled with hydrochloric acid, it is decomposed into phthalic acid and *diamidoethylsulphone*, the *hydrochloride* of which, $SO_2(C_2H_4{\cdot}NH_2)_2,2HCl$, is obtained by filtering and concentrating the solution. The *platinochloride*, $SO_2(C_2H_4{\cdot}NH_2)_2,H_2PtCl_6$, forms sparingly soluble, orange-red, hexagonal tables. The *picrate*, $SO_2(C_2H_4{\cdot}NH_2)_2,2C_6H_3N_3O_7$, crystallises in long needles softening above 170° and melting at 185°.

C. F. B.

δ-Chlorobutylamine, and a Synthesis of Pyrrolidine. By S. Gabriel (*Ber.*, **24**, 3231—3235).—δ-Chlorobutylamine may be prepared from γ-chlorobutyronitrile in the following manner :—35 grams of γ-chlorobutyronitrile is mixed with 32 grams of phenol, and added to a solution of 8 grams of sodium in 100 grams of alcohol. After boiling for an hour, the alcohol is distilled off, water added, and the oily layer which separates taken up with ether and fractionated; the fraction boiling at 285—290° consists of *γ-phenoxybutyronitrile*, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, and solidifies on cooling to crystals melting at 45—46°. The same compound has been obtained by Lohmann from γ-bromopropyl phenyl ether (Abstr., 1891, 1467). On reduction with sodium in alcoholic solution, this compound yields *δ-phenoxybutylamine*, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, a colourless, alkaline oil, boiling at 254—257°, which is converted by hydrochloric acid at 180—185° into phenol and *δ-chlorobutylamine hydrochloride*,

$$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,HCl.$$

The former is extracted with ether, and the acid aqueous solution evaporated; the oily residue solidifies after some time to a crystalline mass which deliquesces in the air, and may be purified by dissolving it in hot amyl alcohol and adding ethyl acetate. The *picrate*, $C_4H_{10}NCl,C_6H_3N_3O_7$, forms amber-yellow, oblique prisms or plates, and melts at 120—121°; and the *platinochloride*, $(C_4H_{10}NCl)_2,H_2PtCl_6$, crystallises in orange scales.

When δ-chlorobutylamine hydrochloride is treated with more than 2 mols. alkali in aqueous solution, and steam passed through the liquid, a base distils over, having an odour closely allied to that of piperidine; it boils at 87·5—88·5°, has the sp. gr. 0·8520 at 22·5°, mixes with water forming a strongly alkaline solution, and fumes in

the air. Its *platinochloride*, $(C_4NH_9)_2,H_2PtCl_6$, crystallises in compact, yellowish-red prisms, which become dark at 190°, and melt at about 200°; the *aurochloride*, $C_4NH_9,HAuCl_4$, becomes plastic at 200° and melts at 205—206° with decomposition; the *picrate*, $C_4NH_9,C_6H_3N_3O_7$, becomes plastic at 105°, and melts at 111—112°; and the *cadmioiodide*, $(C_4NH_9)_2,H_2CdI_4$, forms long, silky needles which become plastic at 210°, and melt at 217—219°. These properties agree, except in the case of the cadmioiodide, with those ascribed by Ladenburg (Abstr., 1886, 528; 1887, 499, 1052) and by Petersen (Abstr., 1888, 498) to pyrrolidine, with which it must therefore be identical. That it is not the isomeric butallylamine, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, is shown by the fact that it does not decolorise bromine-water in acid solution.

H. G. C.

Action of Nitrous Acid on Nonylamine. By M. Freund and F. Schönfeld (*Ber.*, **24**, 3350—3366).—Methylhexylcarbinol is prepared by heating castor oil (100 parts) with 15 per cent potash (150 parts) for half an hour; water (200 parts) is then added gradually, and after remaining for some time the product crystallises. These crystals (500 grams) are mixed with finely powdered potassium hydroxide (170 grams), and the whole rapidly distilled; the distillate is finally dried over potassium hydroxide and fractionated. The pure alcohol boils at 176·5—177°. The iodide is obtained by treating the alcohol with hydrogen iodide at 60°; the yield is almost quantitative. The cyanide, $CN{\cdot}CHMe{\cdot}C_6H_{13}$, is formed from the iodide by the action of potassium cyanide; the actual yield is 14—15 per cent. of the theoretical. It is suggested by the authors that methyl cyanide should be termed *carbin cyanide*, and that the names of the higher homologues should be derived from this in a similar manner to that prevailing in the case of the alcohols; the above compound would therefore be termed *methylhexylcarbin cyanide*.

Nonenylamidoxime, $NH_2{\cdot}C(:NOH){\cdot}C_8H_{17}$, is prepared by the action of hydroxylamine hydrochloride and sodium ethoxide on the preceding compound; it crystallises from light petroleum in short, square prisms, and melts at 84°.

Nonylamine, $NH_2{\cdot}CH_2{\cdot}CHMe{\cdot}C_6H_{13}$, is obtained by the reduction of the cyanide with sodium in alcoholic solution, and is purified by means of the hydrochloride; it is a colourless liquid with a fishy odour, and boils at 185—186°. The *hydrochloride* crystallises from light petroleum, and melts at about 130°; the *platinochloride* is deposited from its alcoholic solution in yellow needles.

Nonyldithiocarbamic acid is deposited in crystals on mixing nonylamine with carbon bisulphide.

Nonylcarbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_9H_{19}$, crystallises from water in colourless, lustrous, square prisms which melt at 92°. *Dinonyloxamide*, prepared by the action of nonylamine on ethyl oxalate in ethereal solution, crystallises from alcohol in small, colourless needles, and melts at 92°.

Phenylnonylcarbamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_9H_{19}$, is deposited from dilute alcohol in groups of long, prismatic crystals, and melts at 63°.

Phenylnonylthiocarbamide, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_9H_{19}$, crystallises from dilute alcohol in small plates, and melts at 58—60°.

Nonylamine hydrochloride in aqueous solution is digested with argentic nitrite in excess at temperatures below 50°, and the clear solution distilled; nitrogen is evolved, and on drying and fractionating the distillate, two portions are obtained, the one boiling at 135—150°, the other at 170—192°. The lower fraction consists of *β-methylhexylethylene*, $CH_2{:}CMe{\cdot}C_6H_{13}$; it boils at 141·5—143°, has the sp. gr. = 0·7318 at 11°/11°, and readily absorbs bromine at ordinary temperatures. The constitution of the compound is shown by the mode of its formation. The higher boiling portion of the distillate proved to be *dimethylhexylcarbinol*, $C_6H_{13}{\cdot}CMe_2{\cdot}OH$; this boils at 183—184°, has a sp. gr. of 0·8211 at 12°/12°, and combines with barium oxide. The yield of alcohol is increased by allowing the mixture of nonylamine hydrochloride and argentic nitrite to remain for three days at the ordinary temperature, the reaction being then completed by gently warming.

On oxidation with dilute sulphuric acid and potassium dichromate, dimethylhexylcarbinol yields carbonic anhydride, acetic acid, and caproic acid, thus proving its constitution; with hydrogen iodide, the corresponding *iodide*, $C_6H_{13}{\cdot}CMe_2I$, is formed, and yields, on heating with alcoholic potash, a hydrocarbon which boils at 140—144°; whether the latter is identical with the one described above (b. p. 141·5—143°), or whether it is *α-dimethylheptylethylene*, $CMe_2{:}CH{:}C_5H_{11}$, could not be determined. J. B. T.

Formation of Tetralkylammonium Iodides. By H. Malbot and A. Malbot (*Compt. rend.*, **113**, 554—556).—The three types of reaction between amines and ethereal salts pointed out by one of the authors do not appear to depend on the nature of the alcohols from which the salts and amines are derived. Trimethylamine reacts in the cold with normal propyl iodide, primary isobutyl iodide, primary isoamyl iodide, primary allyl iodide, and secondary isopropyl iodide. The reaction proceeds comparatively rapidly, but is favoured by heating to 100°.

The solutions of the tetralkylammonium iodides formed are precipitated when added to potash; they are not decomposed by boiling with the latter. With silver oxide (not necessarily freshly prepared), they all yield hydroxides. The platinochlorides are generally insoluble in alcohol.

Normal propyl iodide reacts with methylamine more rapidly than isoamyl iodide, and still more rapidly than isobutyl iodide. Isopropyl iodide, although secondary, reacts more rapidly than primary isobutyl iodide. With allyl iodide, the reaction is very violent, like its reaction with bromine.

The union between certain systems of amines and ethereal salts is accompanied by elimination of hydrocarbons, due not so much to the decomposition of the ethereal salt by heat as to a new type of reaction occurring, which corresponds with a greater development of energy (compare *Ann. Chim. Phys.* [6], **13**, 451). W. T.

Benzoyl Derivatives of Glucosamine. By G. Pum (*Monatsh.* **12**, 435—440).—The author confirms the statement of Kueny (Abstr. 1890, 578), that glucosamine hydrochloride does not form benzoyl derivatives when it is heated for a long time with excess of benzoic anhydride.

Pentabenzoyl glucosamine, $C_6H_8Bz_5NO_5$, is obtained when glucosamine hydrochloride (15 grams) is dissolved in water (60 parts), and the solution shaken with 10 per cent. sodium hydroxide (420 c.c.) and benzoic chloride (60 c.c.). It crystallises in snow-white, slender needles, is insoluble in water, dissolves in hot alcohol and acetic acid, and is reconverted into glucosamine hydrochloride and benzoic acid when treated with concentrated hydrochloric acid. The pure substance melts at 203°; but the author found that, on recrystallising from acetic acid the crude product obtained in one operation, a melting point of 215° was shown. The substance of higher melting point does not appear to differ in composition from that which melts at a lower temperature (compare Kueny, *loc. cit.*). G. T. M.

Chloralimide. By R. Schiff (*Gazzetta*, **21**, 490—497).—Pinner and Fuchs (Abstr., 1877, 584), by the action of ammonium acetate on chloral hydrate, obtained a substance of very indefinite melting point which they supposed to be chloralimide, $CCl_3{\cdot}CH{:}NH$. The author finds this to be a mixture.

Chloral hydrate (3 parts) and ammonium acetate (2 parts) are fused together on the water-bath, the product cooled, and then poured into water; about one-fifth of the mass remains undissolved as a yellow solid. On crystallising this from alcohol, Pinner and Fuchs' chloralimide is obtained; it begins to melt at 80°, and finally melts with decomposition towards 200°. On fractional crystallisation from alcohol, it is split into three distinct compounds melting at 146°, 97°, and 225° respectively. If the heating on the water-bath in the preparation of the mixture be too prolonged, the substance melting at 97° cannot be detected in the product.

The compound melting at 146°, on analysis and determination of its molecular weight by the cryoscopic method in acetic acid solution, is found to be *trimolecular chloralimide*, $(CCl_3{\cdot}CH{:}NH)_3$.

The substance melting at 97° is, in a similar manner, found to be *dimolecular chloralimide*, $(CCl_3{\cdot}CH{:}NH)_2$; on heating to above 146°, it is wholly converted into the trimolecular compound. When the trimolecular compound is heated with acetic anhydride, colourless needles, sparingly soluble in the usual solvents, and melting with decomposition at 235°, are obtained. This is *trimolecular diacetylchloralammonia*, $[CCl_3{\cdot}CH(OAc){\cdot}NHAc]_3$; the mother liquors contain the simple diacetylchloralammonia previously described by the author (Abstr., 1877, 308). When dimolecular chloralimide is employed in place of the trimolecular compound, the same products are obtained.

The compound melting with decomposition at 225° has the composition $C_6H_6Cl_5N_3O$, and seems to be formed by the mutual action of trimolecular chloralimide and ammonium acetate. W. J. P.

Amidoximes and Azoximes. By F. Tiemann (*Ber.*, **24**, 3420—3426).—This paper is an introduction to the following papers. The author has observed that the reaction between orthocyanobenzyl cyanide and hydroxylamine is not normal. Under varying conditions, only 1 mol. of hydroxylamine reacts with 1 mol. of orthocyanobenzyl cyanide, and the product of the reaction does not behave like an amidoxime containing an intact cyano-group, but has properties which show that the cyano- and amidoxime-groups have reacted on each other. The author puts forward two possible formulæ for this compound, $NH{:}C<\begin{matrix}C_6H_4\cdot CH_2\\ O\text{——}N\end{matrix}>C\cdot NH_2$ and $NH_2\cdot C<\begin{matrix}C_6H_4\cdot CH_2\\ NH\\ O\text{——}N\end{matrix}>C$.

An examination of the amidoximes shows that scarcely one, when prepared from the corresponding nitrile, can be isolated as such, since the amidoxime group at once reacts with another group which is present. Thus, hydroxylamine and ethyl orthocyanobenzoate do not react to form ethyl benzenylamidoximeorthocarboxylate,

$$COOEt\cdot C_6H_4\cdot C(NOH)\cdot NH_2,$$

but alcohol is eliminated, and phthalimidoxime, $CO<\begin{matrix}C_6H_4\\ NH\end{matrix}>C{:}NOH$, is produced. The latter is easily converted into phthalimide by the action of ferric chloride and hydrochloric acid, or of nitrous acid.

Rosenthal (*Ber.*, **22**, 2983) has shown that hydroxylamine reacts with a cyano-group contained in a carbon side chain, rather than with one in the benzene nucleus. Hence, orthocyanobenzyl cyanide should first yield orthocyanophenylethenylamidoxime, $CN\cdot C_6H_4\cdot CH_2\cdot C(NOH)\cdot NH_2$, from which a compound of the formula $NH{:}C<\begin{matrix}C_6H_4\cdot CH_2\\ NH\text{——}\end{matrix}>C{:}NOH$ would be formed.

If the latter compound were then converted into a stable isomeride which does not contain a free oximido-group, does not lose ammonia under the action of acids and bases, and has slight basic properties, this compound will probably have the constitution expressed by the second formula given above. The author reserves the further consideration of this compound for a later date.

In conjunction with F. Garny, he brings forward results in support of the above views.

Trimethylene cyanide is converted by hydroxylamine at 60—70° into the normal products, that is, glutarendiamidoxime,

$$NH_2\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(NOH)\cdot NH_2,$$

and glutarenimidodioxime, $OH\cdot N{:}C<\begin{matrix}C_3H_6\\ NH\end{matrix}>C{:}N\cdot OH$.

If, however, molecular proportions are used, and the action is allowed to take place at the ordinary temperature, a compound is formed similar to that described above as obtained from orthocyanobenzyl cyanide. The author expresses the constitution of this compound by the formula $NH_2\cdot C<\begin{matrix}C_3H_6\\ NH\\ O\text{–}N\end{matrix}>C$.

If the reaction takes place at a somewhat higher temperature, ammonia is evolved, and glutarimidoxime, $CO<\begin{matrix}C_3H_6\\NH\end{matrix}>C{:}NOH$, is formed.

Ethylene cyanide and hydroxylamine react in molecular proportion to yield succinimidoxime, $CO<\begin{matrix}C_2H_4\\NH\end{matrix}>C{:}NOH$, just as glutarimidoxime is formed from trimethylene cyanide.

Succinimidoxime is also easily obtained by the action of nitrous acid (1 mol.) on succinenimidodioxime; by the further action of nitrous acid, succinimide is obtained. The author points out that this reaction supports the formula $\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>NH$ for succinimide.

Glutarimidoxime is obtained in an analogous way from glutarenimidodioxime.

In the glutaric series, the tendency to ring formation is so great that glutarimidoxime is produced by replacing an oximido-group in glutarendiamidoxime by oxygen, and evaporating the solution of butenylamidoximecarboxylamide so produced.

Succinimidoxime cannot be prepared in this way. By the action of hydroxylamine on succinimide, succinaminehydroxamic acid is first formed, and then 2 mols. condense to form disuccinimidodihydroxamic acid, $NH(CO\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot OH)_2$.

In conjunction with H. Modeen, the author has examined the action of hydroxylamine on ethyl cyanacetate, and finds that the product consists of methenylamidoximacetohydroxamic acid,

$$OH\cdot N{:}C(NH_2)\cdot CH_2\cdot CO\cdot NH\cdot OH,$$

a compound which is both an amidoxime and hydroxamic acid.

Finally, in conjunction with L. Michaelis, the author has prepared nicotenylamidoxime, $C_5NH_4\cdot C(NH_2){:}NOH$ (see this vol., p. 206), from β-cyanopyridine. It is more stable than the aliphatic amidoximes, and behaves like benzenylamidoxime. E. C. R.

Action of Hydroxylamine on Derivatives of Succinic and Glutaric Acids. By F. Garny (*Ber.*, **24**, 3426—3437).—Ethylene cyanide, the compound from which the first series of compounds described in this paper is derived, is prepared according to Pinner's method, by heating equal weights of ethylene bromide and potassium cyanide in alcoholic solution for two hours in a reflux apparatus on the water-bath. The mixture is kept neutral by successive additions of dilute sulphuric acid. The product is then fractionally distilled.

Succinimidoxime, $CO<\begin{matrix}C_2H_4\\NH\end{matrix}>C{:}NOH$, is prepared by digesting ethylene cyanide (1 mol.), dissolved in alcohol, with an aqueous solution of hydroxylyamine hydrochloride (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) for eight hours at 60—70° in a closed vessel; on evaporating the solution to dryness, ammonia is evolved; the residue is extracted with absolute alcohol and filtered hot. On cooling, the

compound separates in white crystals, melts at about 197° with decomposition, and turns brown before melting. It is soluble in water, sparingly so in hot alcohol, insoluble in ether, benzene, light petroleum, and chloroform, has both acid and basic properties, and dissolves in sodium hydroxide solution with a bluish-green coloration. The *hydrochloride* is soluble in alcohol, crystallises in radiating needles, and melts at 98°. The *picrate* is precipitated on allowing a concentrated solution of succinimidoxime and picric acid to remain some time, and melts at 212°. Silver nitrate gives no precipitate. The *copper* salt is moss-green; the *lead* salt white. With ferric chloride, it gives a reddish-brown coloration; when boiled with Fehling's solution, a reddish-brown, crystalline precipitate is obtained. It is converted into succinimide on adding sodium nitrite to an aqueous solution and then gradually adding hydrochloric acid to the well-cooled mixture.

Succinimidoxime is also prepared by the following methods :—

1. Drouin (*Compt. rend.*, **108**, 675) has obtained the nitrile of succinaminic acid by heating ethylene cyanide with alcoholic ammonia at 110°. This nitrile is treated with hydroxylamine hydrochloride, as described above; on evaporating the solution to dryness, ammonia is evolved, and on extracting the residue with absolute alcohol succinimidoxime is obtained.

2. Sembritzki (*Ber.*, **22**, 2958) has obtained succinendiamidoxime (m. p. 188°) by the action of hydroxylamine (2 mols.) on ethylene cyanide at the ordinary temperature; if, however, the mixture be heated, ammonia is eliminated and succinenimidodioxime is produced. The latter contains 2 mols. of water of crystallisation, and melts at 207°; after drying, it melts at 198°. Succinimidoxime is obtained by adding sodium nitrite (1 mol.) to this product, dissolved in hydrochloric acid.

Succinendiamidoxime is produced by the action of hydroxylamine (1 mol.) on ethylene cyanide (1 mol.) in the cold.

In the hope of preventing the hydrolysis of the succinimidoxime, which takes place when it is prepared according to the first method given above, ethylene cyanide dissolved in absolute alcohol was digested in a closed vessel for eight hours at 70° with hydroxylamine hydrochloride dissolved in absolute alcohol, and the quantity of sodium ethoxide required to neutralise the hydrochloric acid. But under these conditions succinendiamidoxime is formed.

The author draws attention to the fact that, although the mixture was heated, ammonia is not eliminated from both amidoxime groups; only a very small quantity of succinenimidodioxime could be detected.

Benzoylsuccinimidoxime, $CO<\begin{matrix}C_2H_4\\NH\end{matrix}>C{:}NOBz$, is obtained by adding the equivalent quantity of benzoic chloride to succinimidoxime, dissolved in the calculated quantity of sodium hydroxide. The mixture is shaken as long as the odour of benzoic chloride can be detected, and then allowed to remain for 12 hours with dilute ammonia, in order to remove the benzoic acid which is formed. The precipitate is collected, dissolved in chloroform, and precipitated with petroleum,

and finally crystallised from chloroform. It forms a white powder, melts at 184°, is soluble in alcohol, benzene, and chloroform, sparingly so in ether, and insoluble in water and light petroleum. It dissolves in hydrochloric acid, but not in potassium hydroxide.

Glutarimidoxime, $CO<\begin{matrix}C_3H_6\\NH\end{matrix}>C{:}NOH$.—Trimethylene cyanide, from which this compound is obtained, is prepared in the same way as ethylene cyanide, but the action is much slower.

Biedermann (*Ber.*, **22**, 2967) obtained glutarendiamidoxime (m. p. 233°) and glutarenimidodioxime (m. p. 193°) by the action of 2 mols. of hydroxylamine on trimethylene cyanide at 60—70°. By the action of 1 mol. of hydroxylamine on trimethylene cyanide at the ordinary temperature, he obtained a compound which is isomeric with γ-cyanobutenylamidoxime, and melts at 103°.

In order to obtain a compound of the glutaric series analogous to succinimidoxime, trimethylene cyanide (1 mol.) is digested in a closed vessel with hydroxylamine (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) in dilute alcohol for eight hours at 60—70°. On cooling, a precipitate is obtained, which consists mainly of glutarendiamidoxime. Ammonia is evolved when the filtrate is evaporated to dryness, and glutarimidoxime is obtained by extracting the residue with absolute alcohol. It melts at 196°, is soluble in hot water and alcohol, almost insoluble in ether, benzene, light petroleum, and chloroform, and dissolves both in hydrochloric acid and potassium hydroxide. Silver nitrate gives no precipitate. The *copper* salt is bright green; the *lead* salt white. With ferric chloride, it gives a brown, with Fehling's solution a green coloration, but no precipitate is formed. When dissolved in hydrochloric acid and treated with the calculated quantity of sodium nitrite, it yields glutarimide; the latter crystallises from alcohol and melts at 152°.

Glutarimidoxime can also be prepared by treating glutarendiamidoxime dissolved in hydrochloric acid with sodium nitrite.

The compound melting at 103°, and described by Biedermann, is not formed under the above conditions.

Benzoylglutarimidoxime is obtained in the same way as benzoylsuccinimidoxime. It crystallises from alcohol in needles, melts at 160°, and is soluble in alcohol, benzene, and chloroform, almost insoluble in ether, and insoluble in water and light petroleum. It dissolves in hydrochloric acid, but not in potassium hydroxide.

Disuccinimidodihydroxamic acid, $NH{\cdot}(CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}OH)_2$, is obtained by digesting succinimide (1 mol.) with hydroxylamine hydrochloride (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) at 60—70°. The product is evaporated to dryness and extracted with alcohol; on allowing the alcohol to evaporate slowly, beautiful, lustrous needles of the new compound are obtained. It melts at 171°, is very soluble in water, less so in hot alcohol, and only sparingly in ether; it is insoluble in benzene, light petroleum, and chloroform. The aqueous solution has an acid reaction. With ferric chloride, it gives an intense, dark cherry-red coloration, characteristic of the hydroxamic acids. The vapour density cannot be determined, as the substance decomposes when heated above its melting point; neither can the molecular

weight be determined by Raoult's method. The *silver* salt is white, but rapidly blackens in the air. The *sodium* salt is formed by adding sodium ethoxide to an alcoholic solution of the acid. The *copper* salt is bright green, the *lead* salt white. When boiled with hydrochloric acid, it is converted into succinic acid. The *picrate* forms yellow needles, and melts at 266°. The *tetrabenzoyl* derivative melts at 123°, and is soluble in alcohol, ether, benzene, light petroleum, and chloroform, very sparingly so in hot water.

In the hope of obtaining succinhydroxamic acid, succinamide was treated at 60—70° with free hydroxylamine (1 mol.), but under these conditions also disuccinimidodihydroxamic acid is formed.

E. C. R.

Action of Hydroxylamine on Ethyl Cyanacetate. By H. Modeen (*Ber.*, **24**, 3437—3439).—Nitriles are converted by hydroxylamine into amidoximes; and certain ethereal salts are converted by hydroxylamine into hydroxamic acids, the ethereal group being eliminated as alcohol. According to Müller (*Ber.*, **18**, 2485, and **19**, 1491), aromatic compounds which are both nitriles and ethereal salts, when treated with hydroxylamine, are converted into amidoximes, and the ethereal group remains unattacked.

The author has examined the behaviour of ethyl cyanacetate, a cyano-ethereal salt of the aliphatic series, with hydroxylamine, and obtains a result quite different from that of Müller.

Methenylamidoximacethydroxamic acid,

$$OH\cdot N{:}C(NH_2)\cdot CH_2\cdot CO\cdot NH\cdot OH,$$

is obtained by heating a clear alcoholic solution of ethyl cyanacetate (30 grams), hydroxylamine hydrochloride (40 grams), and sodium carbonate (82·3 grams) for 3—4 hours at 40°. On cooling, the compound separates in snow-white crystals. It crystallises in well-formed prisms, is insoluble in ether, ethyl and methyl alcohols, light petroleum, benzene, chloroform, carbon bisulphide, acetic acid, and acetone, sparingly soluble in cold water, easily so in hot water, sodium hydroxide, ammonia, and dilute hydrochloric, sulphuric, or nitric acid. It turns brown on heating, decomposes about 150°, and gives off ammonia when heated on platinum foil. The aqueous solution has an acid reaction, gives a deep-red coloration with ferric chloride, and a dirty-coloured precipitate with Fehling's solution.

Methenylamidoximacetohydroxamic acid is also formed by the action of hydroxylamine on ethyl cyanacetate at the ordinary temperature. If hydroxylamine insufficient to decompose the ethereal salt be employed, part of the latter remains unaltered; the rest is converted into the above compound. Hence the cyano- and carboxyethyl-groups are equally attacked. The author has prepared a number of derivatives of the new compound, and hopes to describe them at a later date.

E. C. R.

Saponification by Sodium Ethoxide. By K. Obermüller (*Zeit. physiol. Chem.*, **16**, 152—159; compare Abstr., 1890, 1474; 1891, 1143).—Saponification by sodium ethoxide is more rapid than by the methoxide (which is slowest) or the amyloxide. It was found

that the addition of ether to the mixture stops the process of saponification. The whole process can be divided into two stages, first, a formation of sodium glycerol and an ethyl salt of the fatty acid, which is more easily saponified than the fat; this is saponified by the sodium hydroxide which is formed from the sodium glycerol and the water present. W. D. H.

Metallic Formates. By W. Lossen and G. Voss (*Annalen*, **266**, 33—52).—The statements of Heusser (*Pog. Ann.*, **83**, 37) that barium formate is isomeric with the corresponding manganese, zinc, and copper salts, and that strontium and copper formates are isomeric, are incorrect.

Copper formate crystallises in various forms according to the conditions of the experiment; by slowly evaporating an aqueous solution of the salt at 75—85°, anhydrous crystals are obtained, but at 50—60° monoclinic crystals ($a : b : c = 1{\cdot}33073 : 1 : 1{\cdot}22445$, $\beta = 96° 37'$), having the composition $(CHO_2)_2Cu + 2H_2O$ separate from the solution; when copper formate is crystallised from hot concentrated formic acid, a salt containing 4 mols. H_2O is obtained. The following double salts were prepared:—

$2(CHO_2)_2Ba,(CHO_2)_2Cu + 4H_2O$
$2(CHO_2)_2Ba,(CHO_2)_2Zn + 4H_2O$
$2(CHO_2)_2Ba,(CHO_2)_2Co + 4H_2O$
$2(CHO_2)_2Ba,(CHO_2)_2Ni + 4H_2O$
} Triclinic.

$(CHO_2)_2Ba,(CHO_2)_2Cd + 2H_2O$.
$2(CHO_2)_2Sr,(CHO_2)_2Cu + 8H_2O$. F. S. K.

Propionates. By R. Gaze (*Arch. Pharm.*, **229**, 486—492; compare Abstr., 1887, 654).—Calcium propionate crystallises both in long (7 cm.), transparent needles with 3 mols. H_2O, and in transparent laminæ with 1 mol. H_2O. Barium propionate crystallises with 1 mol. H_2O, as heretofore accepted. Zinc propionate was obtained in anhydrous, tabular crystals; Renard (Abstr., 1887, 654) obtained it in needles with 1 mol. H_2O. Copper propionate crystallises with 1 mol. H_2O. Cadmium propionate crystallises in silky, opaque laminæ, which are stable in air and contain 2 mols. H_2O (compare Renard, *loc. cit.*). Magnesium propionate can be obtained in small crystals with 1 mol. H_2O. Lead propionate was obtained in laminæ which were anhydrous (compare Renard, *loc. cit.*). A table is given comparing the formates, acetates, and propionates as to their water of crystallisation. A. G. B.

Ethyl Acetoacetate. By J. U. Nef (*Annalen*, **266**, 52—138.)—The author has made a very careful study of the reactions which take place on treating ethyl acetoacetate and its sodium derivative with halogens, acid chlorides, and alkyl halogen compounds; he comes to the conclusion that the course of these reactions can only be satisfactorily explained by assuming that ethyl sodacetoacetate has the constitution represented by the formula ONa·CMe:CH·COOEt. This view accounts for the marked similarity in behaviour between ethyl sodacetoacetate

on the one hand and the sodium derivatives of ethyl succinosuccinate and ethyl dihydroxyterephthalate on the other; it has been previously shown that in the last-named compounds the sodium is directly combined with oxygen.

An important fact in considering the constitution of ethyl sodacetoacetate is that this substance interacts with alkyl halogen compounds with great energy, and usually at the ordinary temperature. Now if, in such reactions as these, the sodium is directly displaced by the alkyl radicle, the reaction should be even more energetic in the case of the copper, lead, or mercury derivative of ethyl acetoacetate. As a matter of fact, this is not the case; solutions of the copper and lead derivatives, for example, do not react with ethyl iodide even at 100°, and do so only very slowly at 130°. This fact alone renders it probable that no direct substitution of the sodium takes place, and a study of the action of bromine on ethyl sodacetoacetate proved the correctness of this view (see below). It was also found that no simple replacement of sodium takes place when ethyl sodacetoacetate is treated with acid chlorides or alkyl halogen compounds; in the case of benzyl chloride, for example, there is first formed a very unstable additive product of the constitution

$$ONa\cdot CMeCl\cdot CH(CH_2Ph)\cdot COOEt,$$

which immediately loses 1 mol. of hydrogen chloride with formation of ethyl sodiobenzylacetoacetate, $ONa\cdot CMe{:}C(CH_2Ph)\cdot COOEt$; the hydrogen chloride produced in this way reacts with the two sodium derivatives now present, and to the greater extent with that of the substance having the less powerful acid properties, so that ethyl benzylacetoacetate and smaller quantities of ethyl acetoacetate are formed. Some of the ethyl sodiobenzylacetoacetate also combines directly with a further quantity of benzyl chloride yielding a compound of the constitution $ONa\cdot CMeCl\cdot C(CH_2Ph)_2\cdot COOEt$, which is finally converted into ethyl dibenzylacetoacetate by the elimination of sodium chloride. If this explanation of the reaction is the true one, then the more negative the group introduced into the molecule of ethyl acetoacetate in the first stage of the reaction the larger must be the proportion of the di-substitution product formed; experiments fully confirmed this conclusion, as will be shown later.

Hitherto it has been found impossible to introduce two acid radicles into the molecule of ethyl acetoacetate; the author shows that such di-substitution products can be obtained by treating metallic derivatives of ethyl acetoacetate with benzoic or acetic chloride, and he discusses at some length the mechanism of these reactions.

The constitution of ethyl acetoacetate is next considered; the behaviour of this compound with phenylhydrazine (see below) and with ammonia and amides and the fact that it has distinctly acid properties all point to its being a hydroxy-compound. The fact that ethyl acetoacetate, and its methyl and ethyl derivatives are not reduced on treatment with sodium in ethereal solution, whereas the diethyl derivative, which is a true ketone, is almost completely converted into ethyl diethylhydroxybutyrate and a pinacone-like substance which is soluble in alkalis, is also strong evidence against the

ketone constitution in the case of the first-named compounds. Furthermore, if ethyl acetoacetate has the ketone constitution, ethyl malonate must have even more strongly marked acid properties; as a matter of fact, it has no acid properties whatever, and does not interact with sodium in absence of alcohol; it also differs from ethyl acetoacetate and the mono-substitution products of the latter in being unacted on by bromine, chlorine, nitrous acid, and fuming nitric acid in the cold. Ethyl acetoacetate is, therefore, in all probability ethyl β-hydroxycrotonate, OH·CMe:CH·COOEt, and its mono-substitution products the corresponding α-substitution products of ethyl β-hydroxycrotonate. These compounds show no tautomerism or desmotropism, and the above view of their constitution accounts satisfactorily for all their reactions; the idea of a labile form may, therefore, be dismissed as regards these substances.

It is interesting to notice to what a great extent the displacement of the α-hydrogen atom affects the behaviour of the hydroxy-group in ethyl acetoacetate; when the substituting group is more positive than hydrogen, the product, ethyl ethylacetoacetate for example, has more marked alcoholic properties. When, on the other hand, the substituting group is strongly negative, the product has a pronounced acid character; the acetyl, benzoyl, and carboxyethyl derivatives of ethyl acetoacetate decompose carbonates, although their ethereal solutions do not react with sodium. This fact led the author to study the action of sodium on ethereal solutions of various acids; he found that in the case of mellitic, phthalic, succinic, and cinnamic acids there is no reaction, whilst with benzoic acid and picric acid a slight reaction takes place, probably owing to the presence of impurities; an ethereal solution of pure phenol reacts very energetically with sodium.

Ethyl phenyl-β-hydrazocrotonate, $N_2H_2Ph·CMe:CH·COOEt$, can be obtained in a crystalline condition by gradually adding phenylhydrazine (10 grams) to a well-cooled, ethereal solution of ethyl acetoacetate (12·5 grams) containing fused calcium chloride, then washing the solution with 10 per cent. soda and dilute sulphuric acid successively, drying over calcium chloride, and evaporating over sulphuric acid; the crude product (16 grams) is spread on porous earthenware and then repeatedly washed with light petroleum. The pure compound (11 grams) crystallises in long, colourless needles, melts at 50°, and is very readily soluble in all ordinary organic solvents except light petroleum; its solutions rapidly turn yellow, and even when in a dry condition the hydrazide gradually changes into a yellow, fluorescent oil. It is readily decomposed into its components by concentrated hydrochloric acid, and when heated at 200° in a vacuum, it is converted quantitatively into phenylmethylpyrazolone. When treated with acetic chloride in well-cooled, ethereal solution, it yields an oil which boils at 245—250° under a pressure of 150 mm., and has most probably the constitution expressed by the formula $CH_2:CMe·NAc·NPhAc$.

A compound of the composition $C_{12}H_{13}NO_2$ is obtained in colourless crystals when the hydrazo-derivative just described is dissolved in concentrated sulphuric acid, the solution kept for ten minutes, and

then poured into a large volume of water. This substance crystallises from alcohol in compact, colourless needles, melts at 134°, is very stable, and is, in all probability, an indole derivative; it is only very slowly acted on by boiling alcoholic potash, but when melted with potash, it gives a strong odour of indole; its alcoholic solution gives a deep-red coloration with ferric chloride.

Ethyl phenyl-β-azocrotonate, NPh:N·CMe:CH·COOEt, is formed when an alcoholic solution of the hydrazo-compound is warmed with yellow mercuric oxide; it melts at 51° and is identical with the compound obtained by Bender (Abstr., 1888, 53) by the action of phenylhydrazine on ethyl α-chloracetoacetate.

The ethyl α-bromacetoacetate prepared by Schönbrodt's method (Abstr., 1890, 27) is a pure compound, as is shown by the following facts:—When treated with ethyl sodacetoacetate, it yields only ethyl diacetosuccinate (see below), and on oxidation with fuming nitric acid in the cold, it gives ethyl bromisonitrosoacetate, NOH:CBr·COOEt. The product obtained by treating ethyl acetoacetate with bromine as described by Duisberg (Abstr., 1882, 1193), is not pure ethyl γ-bromacetoacetate, as was supposed by Hantzsch (Abstr., 1890, 1238) and by Steude (Abstr., 1891, 742), but is a mixture of approximately equal quantities of the α- and γ-bromo-derivatives, and contains, in addition, a little dibromo-derivative and some unchanged ethyl acetoacetate; this is proved by the fact that, on oxidation with nitric acid, it yields a mixture of ethyl isonitroso- and ethyl bromisonitrosoacetoacetate, and also by a study of its behaviour with ethyl sodacetoacetate (see below). The product obtained by treating ethyl sodacetoacetate with bromine is also a mixture of the α- and γ-bromo-derivatives; the formation of both these compounds in this way is best explained by supposing that the addition of bromine first takes place, yielding a compound of the constitution ONa·CMeBr·CHBr·COOEt, from which hydrogen bromide is immediately eliminated giving the α-bromo-derivative, ONa·CMe:CBr·COOEt; the hydrogen bromide thus produced acts on a further quantity of ethyl sodacetoacetate with formation of ethyl acetoacetate, which is then attacked by the bromine, yielding both the α- and the γ-bromo-derivatives.

Ethyl α-acetyl-β'-hydroxyhydromuconate,

$$\mathrm{COOEt{\cdot}C(:CMe{\cdot}OH){\cdot}CH_2{\cdot}C(OH):CH{\cdot}COOEt},$$

is formed, together with its isomeride, ethyl diacetosuccinate, and ethyl dihydroxyterephthalate, when an ethereal solution of ethyl bromacetoacetate, prepared by the action of bromine on ethyl acetoacetate (or its sodium derivative) is treated with ethyl sodacetoacetate at the ordinary temperature; after keeping for two hours, the solution is filtered, and the residue repeatedly washed with small quantities of cold water to free it from sodium bromide and traces of ethyl sodacetoacetate. The undissolved substance is a sodium derivative of ethyl acetylhydroxyhydromuconate of the constitution

$$\mathrm{COOEt{\cdot}C(:CMe{\cdot}ONa){\cdot}CH_2{\cdot}C(OH):CH{\cdot}COOEt};$$

it is very sparingly soluble in cold, but more readily in hot water, and it separates from warm alcohol in colourless, granular crystals. On

treatment with dilute sulphuric acid, it is converted into ethyl acetylhydroxyhydromuconate; this compound crystallises from ether in colourless needles, melts at about 65°, and its alcoholic solution gives a blue coloration with ferric chloride; it is very unstable and, on keeping, quickly changes into an oil, probably a furfuran derivative, water being eliminated. The formation of an isomeride of ethyl diaceotsuccinate in the above reaction is a further proof that Duisberg's ethyl bromacetoacetate contains the γ-bromo-derivative.

Ethyl 1 : 2-*methylcarboxyethylpyrrolineacetate*,

$$COOEt\cdot C\lessdot\begin{matrix}CMe\cdot NH\\ ---\\ CH\end{matrix}\gtrdot C\cdot CH_2\cdot COOEt,$$

is obtained when the sodium derivative just described is boiled with a glacial acetic acid solution of ammonium acetate, and the product precipitated with water; it crystallises from dilute alcohol or glacial acetic acid in needles, melts at 186°, and gives the pine-chip reaction in a very marked manner.

Ethyl diacetosuccinate melts at 88°, and is dimorphous; when crystallised slowly, it forms rhombic plates, but when quickly crystallised, it is obtained in needles; the crystals are monosymmetric, $a : b : c = 0{\cdot}85753 : 1 : 0{\cdot}79288$, $\beta = 73° 55'$.

Ethyl α-*bromomethylacetoacetate*, $C_7H_{11}O_3Br$, is obtained, as sole product, when bromine is gradually added to a well-cooled ethereal solution of ethyl sodiomethylacetoacetate; this substance, and not the γ-derivative as is generally supposed, is also the principal product of the action of bromine on ethyl methylacetoacetate. It is a colourless oil, boils at 107° under a pressure of 30 mm. (at 121°, 50 mm.), and is not acted on by fuming nitric acid or by bromine in cold chloroform solution. It is insoluble in soda, and when heated at 100° for six hours in a sealed tube, it is converted into tetric acid, with elimination of ethyl bromide; this acid has probably the constitution represented by the formula

$$CH_2{:}C(OH)\cdot CMe\lessdot\begin{matrix}O\cdot CO\\ CO\cdot O\end{matrix}\gtrdot CMe\cdot C(OH){:}CH_2.$$

Ethyl α-*bromethylacetoacetate*, $C_8H_{13}O_3Br$, is formed from ethyl ethylacetoacetate under the same conditions as those described in the case of the methyl derivative; it is a colourless oil, boiling at 110° under a pressure of 22 mm. (at 131°, 50 mm.). Its behaviour with bromine and with soda resembles that of the methyl derivative; when heated at 100° in a sealed tube, it yields ethyl bromide and pentic acid, the constitution of which is probably analogous to that of tetric acid.

Some experiments are then described, the results of which confirm Elion's statement that there is only one ethyl sodacetoacetate.

The interaction of ethyl sodacetoacetate and benzoic chloride is then discussed, and it is pointed out that about 10 per cent. of ethyl dibenzoylacetoacetate is invariably present in the crude product; the formation of this compound is explained by assuming that an additive product of the constitution $ONa\cdot CMeCl\cdot CHBz\cdot COOEt$ is produced, and that the latter immediately loses 1 mol. of hydrogen chloride, at

the same time (when the double linking is in a sort of nascent state) combining with benzoic chloride to form the di-substitution product; ethyl sodiobenzoylacetoacetate, when once formed, that is to say, when the double binding is no longer nascent, does not react with benzoic chloride.

Ethyl dibenzoylacetoacetate, $C_{20}H_{18}O_5$, is, however, best prepared by adding benzoic chloride (150 grams) to the copper derivative of ethyl acetoacetate (50 grams), which has been previously mixed to a paste with pure ether, and then heating for a short time on the water-bath. The yield of the pure compound is 32 grams. It is decomposed by a cold alcoholic solution of sodium ethoxide, yielding ethyl benzoate, sodium benzoate, ethyl acetoacetate, and condensation products, and when treated with phenylhydrazine, it gives benzoic acid, β-benzoylphenylhydrazine (m. p. 168°), and probably also ethyl acetoacetate.

Ethyl triacetylacetate, $CAc_3{\cdot}COOEt$, is formed in small quantity when ethyl sodacetoacetate suspended in ether is treated with acetic chloride; it is best prepared by adding acetic chloride to the copper derivative of ethyl acetoacetate suspended in ether. It boils at 102° under a pressure of 12 mm. (at 111°, 22 mm.; at 116°, 29 mm.) without decomposition, and under the ordinary atmospheric pressure at 212—214° with slight decomposition; it is volatile with steam, and does not combine with bromine, but it is decomposed by fuming nitric acid in the cold. It exhibits the same behaviour with sodium ethoxide, and with phenylhydrazine, as the dibenzoyl derivative just described.

Ethyl acetylcarbintricarboxylate, $COOEt{\cdot}CAc(COOEt)_2$, is formed, together with ethyl acetylmalonate and regenerated ethyl acetoacetate, by the interaction of ethyl sodacetoacetate and ethyl chlorocarbonate under the usual conditions. It boils at 129° under a pressure of 29 mm., is volatile with steam, is not acted on by cold fuming nitric acid, and does not combine with bromine; when treated with sodium ethoxide, it is decomposed into ethyl sodacetoacetate and ethyl carbonate. The ethyl acetylmalonate formed in the above reaction boils at 120° under a pressure of 17 mm., and is identical with the compound obtained by the action of acetic chloride on ethyl sodiomalonate; it decomposes carbonates, and gives a dark-red coloration with ferric chloride in alcoholic solution, but its ethereal solution is not acted on by sodium.

Ethyl phenylhydrazine-β-carboxylate, $NHPh{\cdot}NH{\cdot}COOEt$, is obtained when ethyl acetylcarbintricarboxylate is treated with phenylhydrazine in ethereal solution; it crystallises in colourless needles melting at 82°.

A compound of the constitution $HgCl{\cdot}O{\cdot}CMe{:}CAc{\cdot}COOEt$ is formed, together with mercuric chloride and an oily product, when acetic chloride is added to the mercury derivative of ethyl acetoacetate suspended in ether; it separates from ether in heavy, colourless, asymmetric crystals, $a : b : c = 1{\cdot}7712 : 1 : 0{\cdot}83292$, melting at 105°.

Constitution of 5-Pyrazolone Derivatives.—A further investigation of Knorr's 1.3-phenylmethylpyrazolone has confirmed the views previously expressed by the author regarding its constitution; the experiments described below, together with the fact that the con-

densation product of ethyl acetoacetate and phenylhydrazine has been shown to be a hydrazo-compound, prove that phenylmethylpyrazolone has the constitution represented by the formula $\begin{matrix}\mathrm{CMe{\cdot}NH}\\ \|\\ \mathrm{CH{-}CO}\end{matrix}\!>\!\mathrm{NPh}$, and that its acid properties are due to the presence of an imido-group.

1 : 2 : 3-*Phenylbenzoylmethylpyrazolone*, $\begin{matrix}\mathrm{CMe{\cdot}NBz}\\ \|\\ \mathrm{CH{-}CO}\end{matrix}\!>\!\mathrm{NPh}$, is formed when an alkaline solution of phenylmethylpyrazolone is shaken with benzoic chloride; it can also be obtained from the silver derivative of the pyrazolone in like manner. It crystallises from dilute alcohol or light petroleum in needles, melts at 75°, and is very readily soluble in all ordinary organic solvents except light petroleum; it is insoluble in water, dilute acids, and alkalis, and is not acted on by nitrous acid, but is decomposed by alcoholic potash and by concentrated sulphuric acid, yielding benzoic acid and phenylmethylpyrazolone.

1 : 2 : 4 : 3-*Phenyldibenzoylmethylpyrazolone*, $\begin{matrix}\mathrm{CMe{\cdot}NBz}\\ \|\\ \mathrm{CBz{-}CO}\end{matrix}\!>\!\mathrm{NPh}$, can be obtained by strongly heating phenylmethylpyrazolone or its benzoyl derivative with benzoic chloride; it crystallises from alcohol in colourless needles, and melts at 157°.

1 : 3 : 4-*Phenylmethylbenzoylpyrazolone*, $\begin{matrix}\mathrm{CMe{\cdot}NH}\\ \|\\ \mathrm{CBz\cdot CO}\end{matrix}\!>\!\mathrm{NPh}$, is produced when the preceding compound is decomposed with cold, concentrated sulphuric acid, or with boiling alcoholic potash; it crystallises from dilute alcohol in yellowish needles, melts at 86°, and is not decomposed by boiling alkalis; when its solution in potash is shaken with benzoic chloride, it is reconverted into the dibenzoyl derivative (m. p. 157°).

1 : 2 : 4 : 3-*Phenylbenzoylbromomethylpyrazolone*, $\begin{matrix}\mathrm{CMe{\cdot}NBz}\\ \|\\ \mathrm{CBr{-}CO}\end{matrix}\!>\!\mathrm{NPh}$, can be prepared by treating the benzoyl derivative (m. p. 75°) described above with a glacial acetic acid solution of bromine, and also by shaking an alkaline solution of 1 : 3 : 4-phenylmethylbromopyrazolone with benzoic chloride; it crystallises from a mixture of ether and light petroleum in long, colourless needles, melts at 82·5°, and is decomposed by concentrated sulphuric acid and by alcoholic potash with elimination of the benzoyl group.

1 : 2 : 3 : 4-*Phenylbenzoyldimethylpyrazolone*, $\begin{matrix}\mathrm{CMe{\cdot}NBz}\\ \|\\ \mathrm{CMe\cdot CO}\end{matrix}\!>\!\mathrm{NPh}$, prepared from phenyldimethylpyrazolone, crystallises from dilute alcohol and light petroleum in long, colourless needles, melts at 99°, and is readily decomposed by concentrated sulphuric acid and by alcoholic potash.

Bis-1 : 2 : 3-*phenylbenzoylmethylpyrazolone*, $C_{31}H_{26}N_4O_4$, obtained by treating an alkaline solution of bis-phenylmethylpyrazolone with benzoic chloride, separates from glacial acetic acid in colourless, granular crystals, melts at 203°, and is insoluble in alcohol; it is decomposed into its components by alcoholic potash, and by concentrated sulphuric acid.

When 1 : 3-phenylmethylpyrazolone (5 grams) is treated with sodium methoxide and methyl iodide, as described by Knorr, it yields not only Knorr's 1 : 3 : 4 : 4-phenyltrimethylpyrazolone (1·15 grams), but also an even larger quantity (1·8 grams) of 1 : 2 : 3-phenyldimethylpyrazolone (antipyrin) and 1 : 2 : 3 : 4-phenyltrimethylpyrazolone (1·4 grams); 1 : 3 : 4-phenyldimethylpyrazolone, under the same conditions, yields approximately equal quantities of 1 : 2 : 3 : 4-phenyltrimethylpyrazolone (methylantipyrin) and 1 : 3 : 4 : 4-phenyltrimethylpyrazolone. These reactions are easily explained if it be assumed that not only is the sodium of the imido-group directly displaced, but also that an addition of methyl iodide takes place at the double linking; this view is borne out by numerous facts.

In conclusion, the author draws attention to other cases of supposed tautomerism and desmotropism, such as those of carbostyril, isatin, &c.; in his opinion, all the reactions of these compounds can be explained without assuming the existence of labile or pseudo-forms.

F. S. K.

Condensation of Levulinic Acid with Aldehydes. By H. Erdmann (*Ber.*, **24**, 3201—3204).—In this paper the author criticises the results of Ludwig and Kehrer's investigation (Abstr., 1891, 1456) on the action of furfuraldehyde on sodium levulinate, and from the corresponding results obtained by him in the case of benzaldehyde, believes that the compound described as *β*-furfurallevulinic acid is in reality *δ-furfurallevulinic acid*,

$$C_4OH_3{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

The anticipation of Ludwig and Kehrer that this compound would yield derivatives of naphthafurfuran will, therefore, probably not be fulfilled, as such compounds could only be formed from the *β*-derivative. It should, however, be converted into dilevulinic acid,

$$C_2H_4(CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH)_2,$$

by the action of hydrochloric acid. H. G. C.

Reduction of Ethyl Oxalacetate. By W. Wislicenus (*Ber.*, **24**, 3416—3417).—Inactive malic acid is obtained by the reduction of ethyl oxalacetate with sodium amalgam in acid solution. The malic acid can be isolated and purified by means of the lead salt; the yield is 50 per cent. of the theoretical. J. B. T.

Reduction of Acetonedicarboxylic Acid. By H. v. Pechmann and K. Jenisch (*Ber.*, **24**, 3250—3252).—*β-Hydroxyglutaric acid*, $OH{\cdot}CH(CH_2{\cdot}COOH)_2$, is obtained by reducing crude acetonedicarboxylic acid containing about 75 per cent. of the pure acid (100 grams) dissolved in water (1200 c.c.) and neutralised with sodium carbonate (180 grams) with 4 per cent. sodium amalgam (900—1000 grams); the reduction extends over two days, the solution being kept at 0° and a current of carbonic anhydride passed through; an excess of hydrochloric acid is then added, and the solution evaporated to dryness, extracted with alcohol, and the brown syrup which is obtained converted into the copper salt by boiling it with dilute

copper acetate solution; the salt is decomposed by hydrogen sulphide and from the aqueous solution of the acid a colourless syrup is obtained which ultimately solidifies, the yield being 50 grams. It slowly separates from its aqueous solution in stellate groups of needles, melts at 95°, and is readily soluble in water and alcohol, but insoluble in other solvents; on distillation under diminished pressure, glutaconic acid is formed, and the same compound is obtained on boiling it with 60 per cent. sulphuric acid. An aqueous solution of the *sodium* salt gives precipitates with silver, lead, mercury, and copper salts, but not with calcium, barium, zinc, and cadmium salts. The *copper* salt is a blue, crystalline precipitate; the *phenylhydrazide*, $C_5H_6O_3(PhN_2H_2)_2$, produced by heating the acid with three times its weight of phenylhydrazine, crystallises from glacial acetic acid in aggregates of delicate needles, and melts at 234—235°. The acid is not identical with that obtained by Simpson (*Annalen*, **133**, 76) from α-dichlorhydrin and potassium cyanide, which is said to melt at 133°, (the melting point of glutaconic acid). When β-hydroxyglutaric acid is heated with eight times its weight of fuming hydriodic acid in a sealed tube at 180° for four hours, glutaric acid is obtained.

A. R. L.

Alkyl Acetonedicarboxylic Acids. By H. v. Pechmann and K. Jenisch (*Ber.*, **24**, 3248—3249.)—It has been pointed out by Dünschmann and v. Pechmann (Abstr., 1891, 674) that the alkyl substitution derivatives of acetonedicarboxylic acid having an asymmetrical structure, are unstable; as, however, the asymmetry of these derivatives can be conceived in a two-fold sense, first in regard to the relative positions in the molecule of the substituents, secondly in regard to the nature of the latter, and as the asymmetrical compounds hitherto examined have complied with both these conditions, an attempt was made to prepare ethyl methylbenzylacetonedicarboxylate, a compound which only possesses asymmetry in respect to the nature of its substituents. When ethyl acetonedicarboxylate is successively ethylated and benzylated, or when the order of the alkylation is reversed, an oily product which does not show a constant boiling point is obtained; on mixing with alcoholic potash, the fractions passing over at every 10° between 215° and 270°, under a pressure of 40 mm., and decomposing the potassium salts with an acid, carbonic anhydride is the chief product, only minute quantities of oily acids incapable of solidification being obtained. This result favours the view that these acids are only stable when they are symmetrical both as regards the position and nature of the substituent alkyl groups.

A. R. L.

Behaviour of Certain Ketonic Acids towards Sodium Hydrogen Sulphite. By O. Hinsberg (*Ber.*, **24**, 3235—3237).—When dihydroxytartaric acid is added to a concentrated aqueous solution of sodium hydrogen sulphite at 80—100°, it dissolves with the evolution of carbonic anhydride, and, on cooling, crystals of the sodium hydrogen sulphite compound of glyoxal separate; attempts to prepare glyoxalic acid by working at a lower temperature (60—70°) were unsuccessful; a small quantity of glyoxal is obtained

when nitrotartaric acid is treated in a similar manner. Pyruvic acid, when heated with a concentrated solution of the sulphite in a sealed tube at 170°, appears to be unaltered; no decomposition products were recognised. Chloracetic acid dissolves in the sulphite solution at the temperature of the water-bath; but does not yield chloracetone; ethyl acetoacetate remains unaltered even when heated with the same solution at 100° for a long time. A. R. L.

Alkaline Citrates. By T. Salzer (*Arch. Pharm.*, **229**, 547—552).—According to the author's rules (Abstr., 1884, 806), normal salts contain more, or at least as much, water of crystallisation as the corresponding acid salts. Heldt, however (*Annalen*, **43**, 157), states that tripotassium citrate crystallises with 1 mol. H_2O, dipotassium citrate is anhydrous, and monopotassium citrate crystallises with 2 mols. H_2O; the author has, therefore, reinvestigated the alkaline citrates.

Monopotassium citrate is anhydrous when crystallised at the ordinary temperature, and dissolves in $\frac{1}{2}$ part of hot water and somewhat more than 2 parts of cold water; when obtained at a low temperature, it crystallises with 2 mols. H_2O. Dipotassium citrate is also anhydrous. Tripotassium citrate is soluble in $\frac{3}{4}$ part of water at 15°; it can be heated at 170° without loss, but at 200°, it loses 1 mol. water of crystallisation.

Monosodium citrate is anhydrous. The author failed to obtain pure disodium citrate. Trisodium citrate crystallises both with 3 and with $5\frac{1}{2}$ mols. H_2O; the former crystals dissolve in about $1\frac{1}{2}$ parts of water at 15°, the latter in about 1 part of water at 25° and $\frac{1}{2}$ part of boiling water. A. G. B.

Formation of Uric Acid from Cyanacetic Acid and Carbamide. By E. Formánek (*Ber.*, **24**, 3419—3420).—Small quantities of uric acid are formed on heating a mixture of carbamide and cyanacetic acid. Cyanacetic acid (0·5 gram) is cautiously heated with carbamide (2 grams) over a Bunsen burner: a continuous stream of gas is evolved from the melted mass, and, on further heating, the mixture solidifies. The solid mass is dissolved in sodium hydroxide, the solution saturated with ammonium chloride and ammonia, a mixture of magnesium mixture and ammoniacal silver solution added, and the whole allowed to remain, filtered, washed with water, and the silver salt decomposed with sodium sulphide. The silver sulphide is filtered off, the filtrate acidified with hydrochloric acid, and evaporated to a small bulk; the uric acid then separates out. 1 gram of cyanacetic acid and 4 grams of carbamide yielded 20—30 milligrams of pure uric acid. E. C. R.

Hydantoïns and Bases derived from them. By W. Marckwald, M. Neumark, and R. Stelzner (*Ber.*, **24**, 3278—3298).—Thiohydantoïns have been known hitherto only in the aromatic series, having been obtained (Aschan, Abstr., 1884, 907) by melting together aromatic thiocarbamides and amido-acids of the fatty series.

No such reaction takes place in the case of the fatty amido-acids.

Probably these do not exist in the free state as $R{\cdot}CH(NH_2){\cdot}COOH$, but as $R{\cdot}CH<^{NH_3}_{CO-}>O$. If, however, an alkaline solution of the acid, which, doubtless, contains the acid in the form of the salt $R{\cdot}CH(NH_2){\cdot}COOM$, is treated with a thiocarbimide, the reaction does occur, and both aromatic and aliphatic thiohydantoïns were obtained by dissolving the amido-acid in an equivalent quantity of concentrated aqueous potash, and adding an equivalent amount of the thiocarbimide in alcoholic solution. On adding hydrochloric acid, the thiohydantoic acid first separates as an oil, which rapidly loses water, and becomes converted into crystals of the thiohydantoïn.

Phenylmethylthiohydantoïn, $CS<^{NPh{\cdot}CO}_{NH\cdot CHMe}$, prepared from phenylthiocarbimide and alanine, is colourless, and melts at 210°; the yellow substance melting at 180°, which Aschan described, was impure.

Orthotolylthiohydantoïn, $CS<^{N(C_6H_4Me){\cdot}CO}_{NH-\!-\!-\!-\!-CH_2}$, from orthotolylthiocarbimide and glycocine, forms white plates melting at 136°, and dissolves easily in acetic acid, chloroform, and benzene, sparingly in ether and light petroleum.

Orthotolylmethylthiohydantoïn, $CS<^{N(C_6H_4Me){\cdot}CO}_{NH-\!-\!-\!-\!-CHMe}$, from orthotolylthiocarbimide and alanine, resembles the last-mentioned compound, and melts at 198°.

1 : 3 : 4-*Xylylmethylthiohydantoïn*, $CS<^{N(C_6H_3Me_2){\cdot}CO}_{NH-\!-\!-\!-\!-CHMe}$, from xylylthiocarbimide ($Me_2 : NCS = 1 : 3 : 4$) and alanine, forms white needles, melts at 165°, and dissolves readily in ether, alcohol, chloroform, and benzene, very sparingly in light petroleum.

α-Naphthylmethylthiohydantoïn, $CS<^{N(C_{10}H_7){\cdot}CO}_{NH-\!-\!-\!-CHMe}$, from α-naphthylthiocarbimide and alanine, melts at 242°, and is but sparingly soluble in most solvents; it dissolves readily, however, in hot acetic acid.

Phenyldimethylthiohydantoïn, $CS<^{NPh{\cdot}CO}_{NH\cdot CMe_2}$, from phenylthiocarbimide and α-amidoisobutyric acid, forms white crystals, melts at 67°, and dissolves readily in most solvents, but only sparingly in water and aqueous alcohol.

Paratolyldimethylthiohydantoïn, $CS<^{N(C_6H_4Me)}_{NH-CMe_2}>CO$, from paratolylthiocarbimide and α-amidoisobutyric acid, melts at 85°, and is rather more soluble than the preceding compound.

Orthotolyldimethylthiohydantoïn, from orthotolylthiocarbimide and α-amidoisobutyric acid, forms colourless needles melting at 175°, and is less readily soluble than the para-compound. It dissolves, however, in hot alcohol, acetic acid, chloroform, and benzene.

Methylthiohydantoïn, $CS<^{NMe\cdot CO}_{NH\cdot CH_2}$, from methylthiocarbimide and glycocine, forms colourless needles melting at 161°; it dissolves readily in ether, alcohol, and hot water, less readily in cold water and chloroform, and only very sparingly in light petroleum.

Dimethylthiohydantoïn, $CS<^{NMe\cdot CO}_{NH\cdot CHMe}$, from methylthiocarbimide and alanine, forms lustrous, rhombic prisms melting at 166·5°, and dissolves readily in all solvents except light petroleum.

Trimethylthiohydantoïn, $CS<^{NMe\cdot CO}_{NH\cdot CMe_2}$, from methylthiocarbimide and α-amidoisobutyric acid, forms white crystals melting at 53°, and less soluble than the preceding compound in most solvents, but more so in light petroleum.

Allylthiohydantoïn, $CS<^{N(C_3H_5)\cdot CO}_{NH\text{——}CH_2}$, from allylthiocarbimide and glycocine, crystallises only with difficulty. It forms white crystals melting at 108°, and dissolves easily in hot water, alcohol, and acetic acid, sparingly in cold water, chloroform, benzene, and light petroleum.

Allylmethylthiohydantoïn, $CS<^{N(C_3H_5)\cdot CO}_{NH\text{——}CHMe}$, from allylthiocarbimide and alanine, crystallises still less readily. It forms colourless crystals melting at 81·5°, and dissolves readily in alcohol, ether, benzene, acetic acid, and particularly so in chloroform, sparingly in cold water and light petroleum.

Incidentally, an improvement on Tiemann and Friedländer's method (Abstr., 1882, 56) for preparing α-amidoisobutyric acid is described. The *sulphate* of this acid, $C_4H_9NO_2,H_2SO_4 + 2H_2O$, was obtained for the first time. It forms long, pointed, lustrous crystals.

The thiohydantoïns described all show the characteristic properties of thiocarbamides. They yield insoluble silver and mercury salts, which readily decompose, forming the metallic sulphides. They dissolve in alkalis, and when the solutions are boiled, salts of the corresponding thiohydantoic acids are formed. But as the first result of the action of the alkali, compounds of another nature are formed, which have not been isolated, but derivatives of which have been prepared. Take as an example the methylthiohydantoïns derived from alanine. These may react according to either of the formulæ $CS<^{NR\cdot CO}_{NH\cdot CHMe}$ and $SH\cdot C<^{NR\cdot CO}_{N\text{—}CHMe}$. When boiled with potash, they react according to the first, yielding salts of methylthiohydantoic acid. But if they are dissolved in potash and methyl iodide is added, they react according to the second formula, and take up two methyl groups. This may give $SMe\cdot C<^{NR\cdot CO}_{N\text{—}CMe_2}$, an imidazolone, or the thiohydantoïn may react in yet another form, $SH\cdot C<^{NR\cdot C\cdot OH}_{N\text{—}CMe}$, of the second of the two formulæ given above,

yielding $SMe<\begin{matrix}NR\cdot C\cdot OMe\\ \|\\ N—CMe\end{matrix}$, an imidazole. In reality, the compound formed has the last formula, for it is different from the substance that is obtained when the dimethylhydantoïn $CS<\begin{matrix}NR\cdot CO\\ |\\ NH\cdot CMe_2\end{matrix}$ (derived from α-amidoisobutyric acid) takes up one methyl group under the same circumstances; this substance must evidently have the formula $SMe\cdot C<\begin{matrix}NR\cdot CO\\ |\\ N—CMe_2\end{matrix}$, and is, in fact, the other compound that might theoretically be formed when the methylhydantoïn takes up two methyl groups. The imidazoles described below were prepared by treating the methylthiohydantoïns derived from alanine with 2 mols. each of potash and methyl iodide in alcoholic solution; the imidazolones by treating the dimethylhydantoïns derived from α-amidoisobutyric acid with 1 mol. each of potash and methyl iodide in alcoholic solution.

ν-Phenyl-α-methoxy-β-methyl-μ-thiomethylimidazole,

$$SMe\cdot C<\begin{matrix}NPh\cdot C\cdot OMe\\ \|\\ N—CMe\end{matrix},$$

forms an oil which can only be obtained in white crystals with great difficulty; it melts at 90°, and dissolves readily in most solvents, sparingly in water. The *hydrochloride*, $C_{12}H_{14}N_2SO,HCl$, forms small, white crystals melting at 140°, and easily soluble in water and alcohol. The *platinochloride*, $(C_{12}H_{14}N_2SO)_2,H_2PtCl_6$, forms yellowish-red crystals, melts with decomposition at 213°, and dissolves readily in water, sparingly in alcohol. The *picrate*, $C_{12}H_{14}N_2SO,C_6H_3N_3O_7$, forms yellow needles melting with decomposition at 192°, and dissolves sparingly in water, readily in alcohol.

ν-Paratolyl-β-methyl-α-methoxy-μ-thiomethylimidazole,

$$SMe\cdot C<\begin{matrix}N(C_6H_4Me)\cdot C\cdot OMe\\ \|\\ N———CMe\end{matrix}$$

resembles the preceding compound; it forms small, white, lustrous plates melting at 109°. The *hydrochloride*, $C_{13}H_{16}N_2SO,HCl$, forms a white, crystalline powder melting at 123°, and is very soluble in water. The *platinochloride* is yellow, and decomposes at 210° without melting. The *picrate* is yellow, and melts at 180°.

ν-Orthotolyl-β-methyl-α-methoxy-μ-thiomethylimidazole,

$$SMe\cdot C<\begin{matrix}N(C_6H_4Me)\cdot COMe\\ \|\\ N———CMe\end{matrix},$$

is more easily obtained crystalline than the two preceding compounds. It forms large, white plates, melts at 118—120°, and dissolves readily in alcohol, ether, chloroform, and benzene, sparingly in water. The *hydrochloride*, $C_{13}H_{16}N_2SO,HCl$, is white, and melts at 120°. The *platinochloride*, $(C_{13}H_{16}N_2SO)_2,H_2PtCl_6$, is orange-red, and decomposes at 205° without melting. The *sulphate* melts at 205°.

The yellow *picrate*, $C_{13}H_{16}N_2SO,C_6H_3N_3O_7$, melts with decomposition at 200°, and dissolves readily in alcohol, sparingly in water.

νβ-Dimethyl-α-methoxy-μ-thiomethylimidazole,

$$SMe\cdot C\lessdot\begin{matrix}NMe\cdot C\cdot OMe\\ \|\\ N{-}{-}CMe\end{matrix}$$

is a liquid. The acid sulphate, $C_7H_{12}N_2SO_4$, forms a white, crystalline powder, soluble in alcohol, insoluble in ether. The *platinochloride*, $(C_7H_{12}N_2SO)_2,H_2PtCl_6$, forms a yellow precipitate.

ν-Phenyl-β-dimethyl-μ-thiomethylimidazolone, $SMe\cdot C\lessdot\begin{matrix}NPh\cdot CO\\ |\\ N{-}{-}CMe_2\end{matrix}$, is a colourless liquid boiling without decomposition at 222—225°. The *hydrochloride*, $C_{12}H_{14}N_2SO,HCl$, is very soluble in water and alcohol. The *platinochloride*, $(C_{12}H_{14}N_2SO)_2,H_2PtCl_6$, forms reddish-yellow needles melting at 132°, and dissolves readily in alcohol, sparingly in water. The *picrate*, $C_{12}H_{14}N_2SO,C_6H_3N_3O_7$, forms dark-yellow prisms melting with decomposition at 174°, and dissolves easily in alcohol and ether, sparingly in water.

ν-Paratolyl-β-dimethyl-μ-thiomethylimidazolone,

$$SMe\cdot C\lessdot\begin{matrix}N(C_6H_4Me)\cdot CO\\ |\\ N{-}{-}{-}{-}{-}{-}{-}{-}CMe_2\end{matrix}$$

forms a colourless oil, which decomposes when distilled. The *sulphate* melts at 210°. The *platinochloride*, $(C_{13}H_{16}N_2SO)_2,H_2PtCl_6$, forms dark-red needles melting at 152°. The *picrate*,

$$C_{13}H_{16}N_2SO,C_6H_3N_3O_7,$$

forms yellow prisms which decompose at 190°.

ν-Orthotolyl-β-dimethyl-μ-thiomethylimidazolone,

$$SMe\cdot C\lessdot\begin{matrix}N(C_6H_4Me)\cdot CO\\ |\\ N{-}{-}{-}{-}{-}{-}{-}{-}CMe_2\end{matrix}$$

is an oil which decomposes when distilled. The white, hygroscopic *hydrochloride*, $C_{13}H_{16}N_2SO,HCl$, melts at 118°; the *acid sulphate* at 108°. The *platinochloride*, $(C_{13}H_{16}N_2SO)_2,H_2PtCl_6$, is reddish-yellow, and dissolves readily in alcohol and ether, sparingly in water. The *picrate*, $C_{13}H_{16}N_2SO,C_6H_3N_3O_7$, forms yellow prisms, melts with decomposition at 212°, and dissolves easily in alcohol, sparingly in water.

νβ-Trimethyl-μ-thiomethylimidazolone, $SMe\cdot C\lessdot\begin{matrix}NMe\cdot CO\\ |\\ N{-}{-}CMe_2\end{matrix}$, is an oil. The yellow *platinochloride*, $(C_7H_{12}N_2SO)_2,H_2PtCl_6$, melts at 150°; the white *acid sulphate*, $C_7H_{13}N_2SO,H_2SO_4$, at 138°. C. F. B.

Chemical and Physiological Relations of Sulphones. Trisulphones. By E. Laves (*Arch. Pharm.*, **229**, 448—456; compare Abstr., 1889, 1232).—Methyldiphenylsulphone phenyl sulphide (Abstr., 1890, 988) melts at 176°; to convert it into the corresponding trisulphone, which melts at 213° (compare *loc. cit.*), it is dissolved in an alkali, saturated with carbonic anhydride, and poured into permanganate solution; the oxidation is complete in two days.

Ethyl trithioacetate, $CMe(SEt)_3$, is obtained by heating ethyl mercaptan (3 mol. proportions) with 20 per cent. aqueous solution of sodium hydroxide (5 mol. proportions) and methyl chloroform ($1\frac{1}{2}$ mol. proportions) in a strong flask at 100° for two or three days. It is a thick oil of unpleasant odour.

Triethylsulphonemethylmethane, $CMe(SO_2Et)_3$, is prepared by dissolving the foregoing compound in a little benzene and shaking it with a 3 per cent. permanganate solution containing half its volume of 3 per cent. sulphuric acid, the mixture being kept cool until the end of the reaction, when it is slightly warmed and the benzene removed by a current of air; the manganese dioxide is dissolved by the addition of sulphurous acid, when the trisulphone remains as an amorphous, white powder. It crystallises from hot alcohol in vitreous, white needles which melt at 140°; it dissolves easily in chloroform, but not in cold alcohol or ether; at 40° it dissolves in 200 parts of water, and at 15° in 500 parts. It is indifferent to alkalis and is very stable; its taste is very bitter, resembling that of quinine.

3 grams of the powdered sulphone were administered to a dog of 9 kilos. body weight; slight symptoms of lassitude were exhibited at the beginning of the second hour and lasted for half an hour, but there was no further important change; the urine of the next night was found to contain 0·9 gram of unaltered trisulphone. The author administered a dose of 1 gram to himself and experienced very slight lassitude, but his pulse fell in the course of an hour from 75 to 60, and after three hours returned to 72; another dose of 1·5 grams, taken four hours after the first, intensified the action; the urine of the following 24 hours contained 0·85 gram of the unaltered trisulphone. It would appear that the greater part of the trisulphone is not decomposed in the organism, and is therefore without action.

A. G. B.

Ethyl Acetothiënoneoxalate. By A. Angeli (*Gazzetta*, **21**, 444—449).—Part of this paper has appeared before (Abstr., 1891, 550).

Acetothiënoneoxalic acid, $C_4SH_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}COOH$, is obtained by dissolving ethyl acetothiënoneoxalate (5 grams) in concentrated sulphuric acid (40 grams) and heating the mixture for a few minutes on the water-bath. The salt is readily soluble, especially on warming. On pouring the product into much cold water, a bulky precipitate of minute, rose-coloured crystals falls; this is recrystallised from dilute alcohol, precipitated several times from its solution in ethyl acetate by light petroleum, and finally crystallised from boiling benzene. The small, yellowish needles thus obtained turn intensely yellow at 150°, become reddish-brown at 170°, and melt with evolution of gas at 180°. The acid dissolves with effervescence in alkali carbonates; it is precipitated from the solution thus obtained by hydrochloric acid, but not by acetic acid. It is readily soluble in alcohol and ethyl acetate, less so in water, only sparingly in benzene and chloroform, and almost insoluble in light petroleum. The solution of the ammonium salt gives an orange-yellow precipitate with silver nitrate, white with mercuric chloride, pale yellow with lead acetate, green, soluble on heating, with copper sulphate, yellowish with barium

nitrate, and dark red with ferric chloride solution. Alkalis decompose the acid into acetothiënone and oxalic acid. W. J. P.

Bromine Carriers. By W. MacKerrow (*Ber.*, **24**, 2939—2947). —The author has already determined that the extraordinary activity of the halogen carrier when one nitro-group is present in the benzene ring entirely fails if two or three nitro-groups are present. In the latter case, the bromine displaces the nitro-group in preference to a hydrogen atom, and then the influence of the halogen carrier induces further bromination.

Metadinitrobenzene, when treated with bromine alone at 230—235°, gives, together with a large proportion of unaltered material, symmetrical tetrabromobenzene and metabromonitrobenzene. The action goes further in the presence of ferric chloride. Dinitrobenzene (10 grams), bromine (1 mol.), and ferric chloride (2 grams) were heated for 14 hours at 180°. The product consisted of a large quantity of unaltered dinitrobenzene with some perbromobenzene. When bromine (3 mols.) and 8—10 grams of ferric chloride are employed and the mixture heated for 24 hours at 180—190° and then for 15 hours at 220°, the product contained hexabromobenzene, *chloropentabromobenzene*, *dichlorotetrabromobenzene*, and some unchanged dinitrobenzene. The two new compounds crystallise in snow-white needles, are very like hexabromobenzene, and are soluble in alcohol, very sparingly so in hot ether, but easily in boiling acetic acid and benzene. When heated on a watch glass, they sublime without melting; heated in a capillary tube, dichlorotetrabromobenzene melts at 277—279°, chloropentabromobenzene at 294—295°. Dichlorotetrabromobenzene is the more easily soluble, and hexabromobenzene less soluble, in benzene.

Since chlorination takes place when ferric chloride is used as a bromine carrier, the author has employed ferric bromide. Dinitrobenzene (10 grams) was heated for 20 hours at 180—190° with ferrous bromide (5 grams) and bromine (3 mols. *plus* the calculated quantity to form ferric bromide). The product consisted of unaltered dinitrobenzene, a minute quantity of a compound melting at 40—50°, and hexabromobenzene.

Symmetrical trinitrobenzene, when heated with bromine (3 mols.) for 30 hours at 230—235°, gave dibromonitrobenzene and an oily product which was not examined. An attempt was then made to prepare monobromodinitrobenzene by heating trinitrobenzene with bromine (1 mol.) for one hour at 200—210°; a large quantity of unaltered trinitrobenzene was recovered, and a product obtained which melted at 75—76°, and seemed to be the monobromo-compound mixed with some dibromonitrobenzene. With bromine and ferric bromide, trinitrobenzene yielded hexabromobenzene. With bromine and ferric chloride, it gave a new tetrachlorodibromobenzene. *Tetrachlorodibromobenzene* is obtained by heating trinitrobenzene (3 grams) with bromine (12 grams) and ferric chloride (5—6 grams) at 230—235° in a sealed tube. The product is washed with water, a small quantity of trinitrobenzene extracted with alcohol, and the residue crystallised from hot benzene. It crystallises in beautiful

white needles, melts at 241—242°, is insoluble in alcohol, sparingly soluble in hot ether, and somewhat easily so in boiling benzene and acetic acid. When heated on a watch glass, it sublimes without melting.

α-Nitronaphthalene and bromine behave in the way already described by Guareschi (*Annalen*, **122**, 184). The presence of ferric chloride seems to be without influence on the reaction.

Picric acid gives, with bromine alone and in the presence of ferric bromide, orthobromorthoparadinitrophenol, melting at 116·5°. With ferric bromide, the reaction is complete in 12 hours at 100°; without, it requires 20 hours heating at 160—170°, and at this higher temperature some tetrabromoquinone is formed.

Bromodinitrobenzene [$Br : NO_2 : NO_2 = 1 : 2 : 4$] is almost unaltered when heated with bromine and ferric bromide for 14 hours at 130—140°. A small quantity of hexabromobenzene is formed, however.

Pyridine, when treated with bromine and ferric chloride, yields dibromopyridine.

Metanitrobenzoic acid, when heated with bromine and ferric bromide for 10 hours at 130—140°, is, for the most part, unaltered.

Since in the above experiments chlorinated compounds are obtained when ferric chloride is employed as a bromine carrier, the author has examined the action of ferric chloride alone on dinitrobenzene. At 180° no action takes place, and at 200—210° the tube burst with a violent explosion. On performing the experiment in open tubes, it was observed that at 210° gas was evolved, and at 230° the evolution of gas was very violent. The gas was found to be a mixture of carbonic anhydride, nitrogen, hydrogen chloride, and chlorine, and the residue consisted of carbon, ferric chloride, ferrous chloride, and ferric oxide. E. C. R.

Condensation Products of Allyl Alcohol with Methylbenzenes. By G. Kraemer and A. Spilker (*Ber.*, **24**, 3164).—In their paper on the condensation products of allyl alcohol with methylated derivatives of benzene (Abstr., 1891, 1462), the authors overlooked the fact that an oily hydrocarbon of high boiling point was obtained by Baeyer (this Journal, 1873, 885) by the condensation of allyl alcohol with mesitylene by means of concentrated sulphuric acid. A. R. L.

Bromo-derivatives of Carvacrol. By G. Mazzara and G. Plancher (*Gazzetta*, **21**, 470—472).—*Dibromocarvacrol*, [$Br : Pr : Br = 1 : 2 : 3$].—Carvacrol (50 grams) is dissolved in glacial acetic acid (50 grams), cooled, and bromine (107 grams) dissolved in glacial acetic acid (120 grams) slowly added; the product is now poured into much water and the heavy oil which separates is steam-distilled. The pure substance is thus obtained as an oil which does not solidify at −18°. On nitration, dibromocarvacrol yields dinitrocarvacrol together with much resin. The *benzoyl* derivative of dibromocarvacrol is obtained by heating it at 160° with benzoyl chloride. The product is washed with potassium carbonate solution, and on repeated crystallisation from alcohol and light petroleum, is obtained in colourless

arallelopipedons melting at 97—98·5°. The substance is very soluble
ı light petroleum, less so in alcohol. When heated with alcoholic
otash, it yields benzoic acid and the potassium salt of dibromo-
ymenecarboxylic acid. W. J. P.

Behaviour of Carvacrol towards Reducing Agents. By E. Lamberger, B. Berlé, and L. Strasser (*Ber.*, **24**, 3208—3212).—Neither phenol nor carvacrol is acted on by alkaline reducing gents, but the latter is attacked by phosphorus and hydriodic acid at 25—235° with formation of a gaseous hydrocarbon, apparently ropane, and an oil consisting mainly of hydrocarbons. The latter, fter repeated fractionation, was resolved into seven fractions, which, ith the exception of the two largest, appear to be mixtures of hydro-ymenes of different composition, containing also in some cases oluene. The two chief fractions boil at 162—163° and 165—168° espectively, and are mobile, pleasant-smelling, colourless liquids, hich in many respects closely resemble menthene. The latter ompound, however, readily combines with 1 mol. HCl, whilst the raction 162—163° only combines with one-sixth of that amount, nd is therefore probably a mixture of several tetrahydrocymenes, one which may possibly be identical with menthene.

Attempts have also been made to reduce phenol by electrolysing its olution in fused potash, but they failed owing to the difficulty of nding any material which would resist the combined action of the sed potash and the electric current. By the electrolysis of a solution phenol in potash and a little water, the authors obtained, in ldition to salicylic acid, a small quantity of xanthone,

$$C_6H_4<^{-O-}_{CO}>C_6H_4.$$

H. G. C.

Preparation of Primary Amines by means of Potassium nthalimide. By S. Gabriel (*Ber.*, **24**, 3104—3107).—Potassium thalimide has been shown to react with halogen derivatives of the llowing classes of compounds:—Hydrocarbons, nitrohydrocarbons, triles, alcohols, and alkoxy-derivatives of phenols, ketones, and hereal salts. So far, only primary haloïd derivatives have been own to react, excepting picryl chloride, $C_6H_3(NO_2)_3Cl$, and desyl omide, CHPhBr·COPh, but it is probable that the halogen in these o compounds is rendered more easily replaceable by the neighbour-od of the negative groups (CO) and (NO_2). To ascertain if condary haloïd derivatives react at all with potassium phthalimide, e action of normal propyl bromide has been compared with that of propyl bromide. The latter substance does react, but much less ndily than the normal compound.

Normal propyl bromide (6 parts) was heated with potassium thalimide (4 parts) for five hours in a sealed tube at 150—160°. e product was boiled with water; *propylphthalimide*,

$$C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2Me,$$

parated on cooling, and was obtained by crystallisation from small

quantities of alcohol in colourless prisms or plates melting at 66° and boiling at 282—283° under a pressure of 756 mm.

Isopropyl bromide was heated in the same way with potassium phthalimide for seven hours at 160—170°, but the potassium salt was not attacked. The tube was then heated for eight hours at 190°. On opening it, an escape of propylene was observed. The contents were boiled with water to expel the excess of bromide, and the insoluble residue powdered, repeatedly treated with dilute aqueous soda, and recrystallised from small quantities of warm alcohol; *isopropylphthalimide*, $C_8H_4O_2{:}N{\cdot}CHMe_2$, was thus obtained in long, colourless needles melting at 85° and boiling at 272—273° under a pressure of 256 mm.

Since isopropylphthalimide is easily converted into isopropylamine, the above-mentioned reaction of isopropyl bromide will afford the most convenient method of preparing the amine, which has hitherto been obtained only by the reduction of isopropylcarbamine.

C. F. B.

Oxidation Products of Paramidophenetoïl (Paraphenetidine). By W. Kinzel (*Arch. Pharm.*, **229**, 329—355).—The specific gravity of paramidophenetoïl is 1·0613 at 15°, and its boiling point is 254·2—254·7° (corr.) at 760 mm.; Liebermann and Kostanecki give the boiling point as 253° (*Ber.*, **17**, 876; Abstr., 1884, 1146), and elsewhere (*Pharm. Centr.*, 1890, 6, 66) it is given as 242·5°.

Seidel (Abstr., 1890, 490) has shown that the dye obtained by oxidising orthamidophenol is triphenodioxazine, $C_{18}H_{10}N_2O_2$.

By oxidising paramidophenetoïl, a brown colouring matter is obtained, which has the formula $C_{24}H_{22}N_2O_5$ and yields evidence of three ethoxyl groups when treated by Zeisel's method; it may therefore be regarded as *triethoxytriphenodioxazine*, $C_{18}H_7(OEt)_3N_2O_2$, but further investigation of the matter is required. It is best obtained by heating a solution of paramidophenetoïl (41·1 grams) with sulphuric acid (83 grams), water (500 c.c.), and a 3 per cent. solution of hydrogen peroxide (680 grams) at 100°, and after some days evaporating with more sulphuric acid and hydrogen peroxide until no more carbonic anhydride is evolved; the crystals which separate are boiled several times with much water, and finally digested twice with 300 grams of alcohol at 60°. 134 grams of paramidophenetoïl yield 57 grams of the dye. The new compound forms a cinnamon-brown, crystalline powder which partially sublimes in iridescent, brown needles. It is a feeble base and, with concentrated mineral acids, yields violet or blue salts which are soluble in excess of the acid with an intensely blue colour; when such solutions are diluted, the original compound is precipitated unchanged. 1 milligram of the compound will impart a sky-blue colour to 1000 c.c. of concentrated sulphuric acid. Triethoxytriphenodioxazine dissolves in about 900 parts of alcohol, more easily in xylene, benzene, aniline, and chloroform, and most easily in glacial acetic acid, from which it will crystallise, and in pyridine; in water and ether it is almost insoluble. The *acetyl* derivative is of uncertain composition; it appears to contain more acetyl than would suffice to replace the three ethoxyl groups. The *platinochloride* is unstable, and dissolves in sulphuric acid with a blue colour. The *leuco*-base, $C_{24}H_{24}N_2O_5$, ob-

ained by heating the dye with xylene and phenylhydrazine (compare eidel, *loc. cit.*), crystallises in microscopic, white needles, which are onverted into the original dye during the process of drying. The *ydrochloride*, $C_{24}H_{22}N_2O_5,2HCl$, forms crystals which are violet by ransmitted light, and nearly black, with a greenish lustre, by reflected ght.

Quinone, carbonic anhydride, acetic acid, oxalic acid, and resinous ubstances are also produced by the oxidation of paramidophenetoïl; hen the oxidation is effected by potassium permanganate in the cold, ie yield of carbonic anhydride and quinone is much less, and parazo-henetoïl melting at 159° (Beilstein, *Handbuch*, gives 157° and 160°) produced to a considerable extent. This is the product of the xidation which gives a blood-red colour with sulphuric acid, and the uthor attributes the red colour of the earlier samples of commercial henacetin to the presence of this substance.

From the mother liquor of the permanganate mixture from which ie parazophenetoïl had crystallised out, brownish needles of a *com-ound* $C_{16}H_{18}N_2O_3 + H_2O$ were obtained; these melted at 178°, and ieir formula corresponds with that of parazoxyphenetoïl. As this ubstance has not yet been described, the author prepared it (see elow), and found that the crystals melting at 178° are not identical ith it; so the constitution of the said crystals is still uncertain, but asmuch as they give the same carmine-red colour with fused chloral ydrate as azoxy-compounds, including parazoxyphenetoïl, generally , there is strong evidence that they are paroxyazophenetoïl.

Parazoxyphenetoïl, $C_{16}H_{18}N_2O_3$, is prepared by reducing paranitro-ienetoïl (5 grams) in 95 per cent. alcohol (100 grams) with 10 per nt. sodium amalgam at 10°, keeping the mixture at 0° for two ours with frequent shaking. When recrystallised, it forms bright-ellow tables which melt at 136·6° (uncorr.), and dissolve easily in ot alcohol.

Parahydrazophenetoïl, obtained by reducing parazophenetoïl with mmonium sulphide in alcohol, crystallises in white needles which elt at 118—119°.

The red colour of commercial carbolic acid is probably to be attri-ted to the presence of the colouring matter described in this paper.

A. G. B.

Action of Nitric Acid on Dimethylorthanisidine (Dimethyl-thomethoxyaniline). By P. VAN ROMBURGH (*Compt. rend.*, **113**, 5—508).—Grimaux and Lefèvre obtained a substance melting at 5° by heating dimethylorthanisidine with ordinary nitric acid and, ien nitrous vapours appeared, immediately precipitating with water. iey gave to this compound the formula

$$OMe\cdot C_6H_2(NO_2)_2\cdot NMe\cdot CH_2\cdot NO_2$$

ompt. rend., **112**, 727). This result appears to differ from what has en observed in connection with other aromatic amines by the author *ec. trav. Chim.*, **3**, 409), and confirmed by Gattermann (*Ber.*, **18**, 32).

The author has prepared the product melting at 135° by the method ven by Grimaux and Lefèvre. It contains 22·2 per cent. of nitrogen;

a substance of the above formula would contain 19·58 per cent. When boiled with phenol, the solution becomes red, and on the addition of alcohol, a reddish-orange product is obtained, melting at 168°. The author has shown that nitramines under these circumstances have a nitro-group displaced by hydrogen (*Rec. trav. Chim.*, **5**, 241); he now finds the same reaction to occur with nitrosamines. The orange-red product is also obtained on boiling the nitramine of dinitromethylorthanisidine with phenol. Its composition is as follows:—

$$OMe\cdot C_6H_2(NO_2)_2\cdot NHMe.$$

To prove that the substance melting at 135° has the composition $OMe\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO$, the author has prepared it from the corresponding nitramine, certainly containing only one methyl group. The preparation melts at 135°, and has the same characters as the substance prepared by the method of Grimaux and Lefèvre. W. T.

Phenacetin. Metethoxyorthophenylenediamine. By W. Autenrieth and O. Hinsberg (*Arch. Pharm.*, **229**, 456—467.)—To distinguish between antifebrin, antipyrin, and phenacetin, the substance is boiled for a short time with 10—12 per cent. nitric acid; under these conditions, phenacetin colours the solution yellow to orange, and an intensely yellow nitro-derivative crystallises on cooling.

Orthonitrophenacetin,

$$NO_2\cdot C_6H_3(OEt)\cdot NH\cdot COMe\ [OEt : NO_2 : NHCOMe = 4 : 2 : 1],$$

is prepared as described above. It crystallises from water in long, soft, silky, yellow needles, melts at 103°, and dissolves in hot water, hot dilute alcohol, absolute alcohol, ether, and chloroform. When dissolved in hot alcohol and boiled for a short time with rather more than the theoretical quantity of potassium hydroxide, it is converted into *orthonitrophenetidine*, $NO_2\cdot C_6H_3(NH_2)\cdot OEt\ [OEt : NO_2 : NH_2 = 4 : 2 : 1]$, which crystallises as the solution cools in brilliant, red, lustrous prisms, melts at 113°, and dissolves in hot alcohol, ether, and chloroform.

Metethoxyorthophenylenediamine, $C_6H_3(NH_2)_2\cdot OEt\ [OEt : (NH_2)_2 = 4 : 2 : 1]$, is prepared by reducing orthonitrophenetidine with zinc-dust in boiling alcoholic soda; the frothing of the solution indicates the end of the reaction; the liquid is filtered and evaporated in hydrogen; the residue is treated with a little water, which separates the diamine as a brown oil; this is washed with water, dried on a porous plate, and distilled. The new compound, when freshly distilled, forms long, white, slender needles, which rapidly resinify and become red or brown in air. From ether, it crystallises in brilliantly lustrous, greyish-white laminæ which are pretty stable when dry. It melts at 71—72° and distils between 294° and 296°; it dissolves partially in water and easily in alcohol, ether, and chloroform; it is a fairly strong base, turns litmus blue, and forms crystalline salts with bibasic acids, of which the *sulphate* and *oxalate* are described.

Metethoxydihydroxyquinoxaline,

$$OEt\cdot C_6H_3<\begin{matrix}N:C\cdot OH\\ |\\ N:C\cdot OH\end{matrix}\ [OEt : N_2 = 6 : 2 : 3],$$

is prepared by heating metethoxyorthophenylenediamine with excess of oxalic acid in an oil-bath at 140—150° for half an hour (compare *Annalen*, **237**, 327), treating the product with sodium hydroxide solution, filtering, and precipitating the quinoxaline from the filtrate by strong hydrochloric acid. It crystallises from alcohol in slender, pale-yellow needles, melts above 280°, and dissolves sparingly in cold water and alcohol, but hardly at all in ether. The *sodium* salt was obtained.

Metethoxydiacetylorthophenylenediamine,

$$OEt{\cdot}C_6H_3(NHAc)_2\ [OEt : (NHAc)_2 = 4 : 2 : 1],$$

obtained from the diamine and acetic anhydride, crystallises from water in lustrous, colourless prisms which melt at 189°; it dissolves sparingly in cold water, but rather better in hot water, alcohol, and ether. The corresponding *dibenzoyl* derivative, $OEt{\cdot}C_6H_3(NHBz)_2$ $[OEt : (NHBz)_2 = 4 : 2 : 1]$, is obtained by shaking an aqueous solution of the diamine with benzoic chloride and excess of sodium hydroxide; it crystallises from alcohol in slender, white needles, melts at 191—192°, and is insoluble in water, but somewhat freely soluble in hot alcohol.

Metethoxydiphenylsulphonorthophenylenediamine,

$$OEt{\cdot}C_6H_3(NH{\cdot}SO_2Ph)_2\ [OEt : (NHSO_2Ph)_2 = 4 : 2 : 1],$$

is obtained when the diamine is shaken with phenylsulphonic chloride and sodium hydroxide (compare Abstr., 1891, 49); the product is dissolved in dilute sodium hydroxide solution, and reprecipitated by strong hydrochloric acid; it crystallises in slender, white needles which melt at 159—160°, and dissolves in alcohol and ether, but not in water. The *diethyl* derivative, $OEt{\cdot}C_6H_3(NEt{\cdot}SO_2Ph)_2$, formed by heating the diphenylsulphone compound with excess of ethyl iodide and sodium hydroxide in a reflux apparatus, crystallises in slender needles, and melts at 121°. A. G. B.

Action of Diazobenzene on Acetonedicarboxylic Acid. By H. v. Pechmann and K. Jenisch (*Ber.*, **24**, 3255—3260).—The action of diazobenzene salts on certain fatty compounds containing a methylene group, the hydrogen atoms of which are displaceable, does not always give rise to compounds of the same type, for example, Japp and Klingemann (Trans., 1888, 521, 538) showed that the so-called benzeneazoacetone from acetoacetic acid and diazobenzene chloride is pyruvaldehydrazone; whilst Beyer and Claisen (Abstr., 1888, 827) obtained azo-compounds by the action of diazobenzene chloride on derivatives of acetone.

Disbenzeneazoacetone, $CO(CH_2{\cdot}N_2Ph)_2$, is produced when crude acetonedicarboxylic acid (50 grams) is dissolved in water (5 parts) cooled to 0°, a solution of diazobenzene chloride (2 mols.) carefully stirred in, and sodium acetate added; the red precipitate is collected, dried, washed with benzene, and crystallised from dilute alcohol, when it separates in stellate groups of yellowish-red needles, and melts at 175—176°. It has both acidic and basic properties in a slight degree, and dissolves in concentrated mineral acids with a violet colour. On

adding concentrated hydrochloric acid to its alcoholic solution, small, blue needles separate which become red on exposure to the air; it is soluble in boiling sodium hydroxide solution; it can be reduced by tin and hydrochloric acid, and when heated with an equal weight of phenylhydrazine at 120° for half an hour, it yields the *hydrazone*, $NHPh{\cdot}N{:}C(CH_2{\cdot}N_2Ph)_2$, which crystallises in hexagonal plates, melts at 166°, and dissolves in concentrated sulphuric acid with a green colour. When the hydrazone is boiled with 3 to 4 times its weight of acetic anhydride, the *pyrazole derivative*, $CMe\lessdot^{NPh—N}_{C(N_2Ph)}\gtrdot C{\cdot}CH_2{\cdot}N_2Ph$, is formed; this crystallises from light petroleum in lustrous, golden plates, and melts at 125°. In conclusion, attention is drawn to the fact that the above-described azo-compound is quite distinct from the compound $C_{15}H_{14}N_4O$, obtained by Bamberger and Wulz (Abstr., 1891, 1449) by the action of acetone on diazobenzene chloride in the presence of alkali. A. R. L.

Action of Phenylhydrazine on Acetonedicarboxylic Acid. By H. v. Pechmann and K. Jenisch (*Ber.*, **24**, 3252—3255).—When a mixture in molecular proportions of crude acetonedicarboxylic acid, dissolved in water (8 parts), concentrated hydrochloric acid, and phenylhydrazine is heated on the water-bath for several hours, and sodium carbonate is added to incipient turbidity, methylphenylpyrazolonecarboxylic acid (Abstr., 1891, 673) separates after a time in crystals, and a further quantity is obtained on adding sodium carbonate to the filtrate. When the last-mentioned acid is heated at 160°, and then distilled under a pressure of 100 mm., Knorr's methylphenylpyrazolone passes over.

When crude acetonedicarboxylic acid (50 grams) is dissolved in a little water, neutralised with sodium carbonate, cooled to 0°, and treated with a solution of phenylhydrazine hydrochloride (2 mols.), in water (400 grams), carbonic anhydride is evolved, and yellowish needles separate; the substance is insoluble in cold water, but soluble in the hot liquid, and is perhaps the *phenylhydrazine salt of the hydrazone of acetoacetic acid*, $N_2HPh{:}CMe{\cdot}CH_2{\cdot}COOH,N_2H_3Ph$. It remains unaltered for several days in the presence of water, but in the dry state decomposes with the evolution of carbonic anhydride yielding an oil of disagreeable odour; when the latter is dissolved in dilute hydrochloric acid, reprecipitated with alkali, and dissolved in 50 per cent. alcohol, the addition of alcoholic oxalic acid causes a precipitate of phenylhydrazine oxalate, whilst acetonephenylhydrazone, boiling at 195—200° (20 mm.), can be extracted from the filtrate by means of ether. A. R. L.

Symmetrical Bisphenylhydrazone of Mesoxaldehyde. By E. Bamberger (*Ber.*, **24**, 3260—3264).—Pyruvaldehydephenylhydrazone is not the sole compound formed from acetoacetic acid and diazobenzene chloride (see Japp and Klingemann, Trans., 1888, 538), the author having separated a compound $C_{15}H_{14}N_2O$, melting at 134—135°, identical with that recently described by himself and Wulz (Abstr., 1891, 1449), by allowing the benzene filtrate

from the crystals of the pyruvaldehydrazone to evaporate, treating the tarry residue with alcohol, and finally crystallising from boiling alcohol. The following facts prove that this compound is *mesoxaldehydebisphenylhydrazone*, $CO(CH{:}N_2HPh)_2$. When an aqueous solution of acetoacetic acid (1 mol.) is treated at 0° with one of diazobenzene chloride (2 mols.), and a large excess of 20 per cent. sodium hydroxide solution cautiously added, the mesoxaldehydebisphenylhydrazone is precipitated; it is the chief product, and the same compound is formed when a concentrated aqueous solution of diazobenzene chloride (1 mol.) is added to pyruvaldehydrazone (1 mol.) dissolved in alcohol. The azo-derivative, $C_{15}H_{14}N_4O$, obtained by v. Pechmann and Jenisch (preceding abstract) from acetonedicarboxylic acid is formed in small quantities simultaneously with the isomeric mesoxaldehydebisphenylhydrazone, and the further investigation of it is being carried on by the author. A. R. L.

Action of Oximes on Diazo-compounds. By J. Mai (*Ber.*, **24**, 3418).—On adding diazobenzene chloride in aqueous solution to benzaldoxime dissolved in soda, a voluminous precipitate is formed which quickly becomes dark yellow; the compound crystallises from a mixture of alcohol and ether, and is colourless when pure. It probably has the formula $PhN_2{\cdot}O{\cdot}N{:}CHPh$, and is to be regarded either as an ether, or as an hydroxylamine anhydride derivative. On treatment with dilute hydrochloric acid, benzaldehyde and diazobenzeneimide are obtained.

Similar compounds are formed from isobenzaldoxime, acetoxime, and ethylaldoxime, and as other diazo-derivatives may be substituted for the diazobenzene chloride, the reaction appears to be a general one. J. B. T.

Molecular Transformations of the Aldoximes. By R. Behrend (*Ber.*, **24**, 3088—3090).—The author (Abstr., 1891, 1032) has obtained α- and β-*paranitrobenzaldoximes* by treating dinitrosoparanitrobenzyl with potash, and found that, while the β-oxime is converted into the α-variety by the action of hydrochloric acid on its ethereal solution, the α-oxime undergoes no corresponding change. He now finds that, as Goldschmidt has informed him by letter, the latter change does take place when an ethereal solution of the α-oxime is saturated with hydrogen chloride, whereas, to convert the β- into the α-oxime, the ethereal solution of the former should be treated with only a moderate amount of hydrogen chloride. C. F. B.

Synthesis of Weselsky's Resorcinol Blue. By R. Nietzki (*Ber.*, **24**, 3366—3369; compare Abstr., 1890, 156).—Resazurin is prepared by dissolving nitrosoresorcinol and resorcinol in molecular proportion in alcohol; the solution is cooled, mixed with finely-divided manganese dioxide (1 mol.), and sulphuric acid (2 mols.) diluted with an equal bulk of water is slowly added, the liquid becomes cherry red, and, as soon as a drop brought on to filter paper gives a pure blue coloration with ammonia, the manganese dioxide is filtered off, and the compound precipitated with water; on treating

the product with soda, green crystals of sodium resazurinate are formed. The mother liquid contains sodium resorufinate. Weselsky's method of preparing resazurin consists in treating resorcinol with a mixture of nitrous and nitric acids; the nitrosoresorcinol, which is probably first formed, immediately condenses with the excess of resorcinol, whilst the nitric acid acts as an oxidising agent, and is reduced to nitrous acid.

The author suggests the formula $C_6H_3O\!<\!\overset{N\cdot O}{\underset{\quad O}{\quad}}\!>\!C_6H_3\cdot OH$ [O:N:O = 1:3:4; OH:O:O = 1:3:4] for resazurin, which differs from resorufin inasmuch as it contains the quinonoxime group instead of the quinonimide radicle; the objection that the formula represents the compound as a ring consisting of 7 atoms may be met by writing the oximido-group $O\!:\!\underset{\|}{N}\cdot H$, with a pentavalent nitrogen atom.

J. B. T.

Aromatic Secondary Chlorocarbamides and Tetra-substituted Carbamides. By S. Paschkowezky (*Ber.*, **24**, 2905—2930). —The author has prepared a number of new aromatic derivatives of carbamide.

Thiodiphenylcarbamic chloride, $S\!<\!\overset{C_6H_4}{\underset{C_6H_4}{\quad}}\!>\!N\cdot COCl$, is prepared by heating thiodiphenylamine (10 grams) dissolved in benzene (250 grams) with twice the theoretical quantity of a 20 per cent. toluene solution of carbonyl chloride for $2\frac{1}{2}$ hours on the water-bath. The yield amounts to 75 per cent. of that required by theory. It crystallises from hot alcohol in small, pale-yellow, lustrous, prismatic needles, from toluene in large, well-formed, greenish prisms, and melts at 171—172°. The crystals belong to the monosymmetric system; $a:b:c = 2{\cdot}3615:1:1{\cdot}4465$. It is sparingly soluble in alcohol and ether, easily so in hot benzene and toluene, sparingly in the cold. At 17·5°, one part dissolves in 219 parts of alcohol (96 per cent.), and in 34 parts of benzene.

Phenyl thiodiphenylcarbamate is obtained by heating an alcoholic solution of the preceding compound with sodium phenoxide on the water-bath. It crystallises from alcohol in white, lustrous needles, melts at 164°, and is soluble in hot alcohol, ether, benzene, and acetic acid. At 16°, one part dissolves in 410 parts of alcohol, and in 50·6 parts of benzene.

Unsymmetrical thiodiphenylcarbamide, $S\!:\!(C_6H_4)_2\!:\!N\cdot CO\cdot NH_2$, is obtained by heating thiodiphenylcarbamic chloride with alcoholic ammonia on the water-bath for two hours. It crystallises in colourless tablets, melts at 201—202°, and dissolves copiously (but with difficulty) in boiling methyl and ethyl alcohols and ether, easily in benzene. At 17·5°, one part dissolves in 331·5 parts of alcohol, and in 48·4 parts of benzene. When heated in a sealed tube with alcoholic ammonia for three hours at 140—150°, it yields thiodiphenylamine and carbamide. The same two substances are formed when it is distilled from a retort into aqueous ammonia.

Thiotriphenylcarbamide, $S\!:\!(C_6H_4)_2\!:\!N\cdot CO\cdot NHPh$, is obtained by heating thiodiphenylcarbamic chloride, dissolved in hot xylene, with a

slight excess of aniline. It crystallises from boiling alcohol in white, lustrous needles which turn red on exposure to air, melts at 168—169°, and dissolves copiously, but with difficulty, in boiling alcohol and ether, easily in benzene and chloroform. At 17·5°, one part dissolves in 387 parts of alcohol, and in 26·7 parts of benzene. When heated with excess of aniline, it is easily converted into diphenylcarbamide and thiodiphenylamine. The same products are formed by heating thiodiphenylcarbamic chloride with excess of aniline.

Dithiotetraphenylcarbamide, $CO[N{:}(C_6H_4)_2{:}S]_2$, is obtained by heating a mixture of thiodiphenylcarbamic chloride with thiodiphenylamine in molecular proportion at 220—260°. It crystallises from a mixture of alcohol and benzene in colourless needles, having a red lustre, melts at 231°, and is very sparingly soluble in alcohol, ether, and acetic acid, copiously in cold, and very easily in hot benzene. At 17°, one part dissolves in 2300 parts of alcohol, and in 24 parts of benzene. It is also formed when thiodiphenylcarbamic chloride is heated with thiodiphenylcarbamide for two hours at 200—280°. When heated with concentrated hydrochloric acid at 240—250°, hydrogen sulphide is produced together with a solid dark-green product. Unlike tetraphenylcarbamide, it does not yield carbon dioxide under these conditions (*Ber.*, **11**, 711).

Monothiotetraphenylcarbamide, $NPh_2{\cdot}CO{\cdot}N{:}(C_6H_4)_2{:}S$, is obtained by heating molecular proportions of thiodiphenylcarbamic chloride and diphenylamine at 220—240° for three hours. The product is purified by dissolving it in benzene and passing hydrogen chloride into the solution, when diphenylamine hydrochloride is precipitated; the filtrate is then evaporated to dryness, and the residue washed with alcohol, and crystallised from hot alcohol. It forms colourless, six-sided plates, softens at 163°, melts at 165°, and is soluble in cold alcohol and ether, easily in cold benzene and boiling alcohol and ether, and very easily in boiling benzene.

Thiotriphenyl-β-naphthylcarbamide, $C_{10}N_7{\cdot}HPh{\cdot}CO{\cdot}N{:}(C_6H_4)_2{:}S$, is obtained by heating thiodiphenylcarbamic chloride with phenyl-β-naphthylamine for three hours at 240—260°. It crystallises from alcohol in greyish-white, nodular aggregates, melts at 169—170°, and is easily soluble in boiling alcohol and ether, very easily so in benzene and acetic acid. At 15°, one part dissolves in 190·7 parts of alcohol, and in 29·5 parts of benzene.

Thiodiphenyldi-β-naphthylcarbamide, $N(C_{10}H_7)_2{\cdot}CO{\cdot}N{:}(C_6H_4)_2{:}S$, obtained from di-β-naphthylamine in a similar manner to the preceding compound, crystallises from a mixture of benzene and alcohol in nodular aggregates, melts at 225°, and is sparingly soluble in boiling alcohol and ether, easily in benzene and acetic acid. One part dissolves, at 16°, in 801 parts of alcohol, and in 181 parts of benzene.

Thiodi-β-naphthylcarbamic chloride, $S{<}\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}{>}N{\cdot}COCl$, is obtained by heating thiodi-β-naphthylamine with carbonyl chloride at 160—170° for five hours. It forms small, white needles, melts at 254—255°, is almost insoluble in cold alcohol, very sparingly soluble in hot alcohol and cold benzene, more so in hot benzene and cold xylene, and easily in boiling xylene. At 16·5°, one part dissolves in 1420 parts

of alcohol, and in 134 parts of benzene. When boiled with alcoholic soda, it yields thiodi-β-naphthylamine.

Phenyl thiodi-β-naphthylcarbamate, $S:(C_{10}H_6)_2:N\cdot COOPh$, is obtained by heating the preceding compound with alcoholic sodium phenoxide; it forms small, greyish-white needles, melts at 215°, and is sparingly soluble in both cold and hot alcohol and ether, cold benzene, and acetic acid, but easily in hot benzene and acetic acid. At 16°, one part dissolves in 489·5 parts of alcohol, and in 83 parts of benzene.

Unsymmetrical thiodi-β-naphthylcarbamide, $S:(C_{10}H_6)_2:N\cdot CO\cdot NH_2$, is obtained by heating thiodi-β-naphthylcarbamic chloride with excess of alcoholic ammonia at 140—145° for three hours; it crystallises from benzene in almost colourless needles, which turn green on exposure to air, decomposes at 215° without melting, and is almost insoluble in cold alcohol, ether, and benzene, sparingly soluble in boiling alcohol and ether, more so in boiling benzene, and easily in xylene.

Thiodi-β-naphthylphenylcarbamide, $S:(C_{10}H_6)_2:N\cdot CO\cdot NHPh$, is obtained by heating thiodi-β-naphthylcarbamic chloride dissolved in xylene with twice the molecular proportion of aniline for ¾ hour in a reflux apparatus. It darkens at 180°, decomposes at 215—220° without melting, and is sparingly soluble in alcohol, ether, and cold benzene, xylene, and chloroform, fairly soluble in hot benzene, and easily so in hot xylene and chloroform. At 17·5°, one part dissolves in 275·2 parts of alcohol, and in 551·5 parts of benzene. When boiled with excess of aniline, it yields thiodi-β-naphthylamine and carbanilide.

Dithiotetra-β-naphthylcarbamide, $CO[N:(C_{10}H_6)_2:S]_2$, is prepared by heating a mixture in molecular proportion of thiodi-β-naphthylcarbamic chloride and thiodi-β-naphthylamine dissolved in xylene at 280° for five hours. It crystallises from benzene in yellowish, lustrous leaflets, melts above 350°, and is very sparingly soluble in cold alcohol, ether, benzene, and acetic acid, sparingly so in the boiling solvents, but easily in hot xylene.

Carbamides containing the group $N:(C_{10}H_6)_2:S$, like thiodi-β-naphthylamine, give a violet coloration with concentrated sulphuric acid.

Ethyl phenyl-β-naphthylcarbamate, $C_{10}H_7\cdot NPh\cdot COOEt$, obtained by the action of sodium ethoxide on phenyl-β-naphthylcarbamic chloride in warm alcoholic solution, crystallises in long, white, silky needles, melts at 93°, and dissolves somewhat easily in cold, easily in hot alcohol and ether, and very easily in cold benzene.

Phenyl phenyl-β-naphthylcarbamate is prepared in a similar way to the preceding salt, crystallises in white needles, melts at 149°, is sparingly soluble in cold alcohol, ether, benzene, and acetic acid, easily so in the hot solvents. At 17°, one part dissolves in 278 parts of alcohol, and in 43·4 parts of benzene.

Symmetrical diphenyldi-β-naphthylcarbamide, $CO(NPh\cdot C_{10}H_7)_2$, is obtained by heating a mixture of phenyl-β-naphthylcarbamic chloride with phenyl-β-naphthylamine in molecular proportion for five hours at 240—260°. It crystallises from alcohol in pale-yellow, polyhedral granules, melts at 185—186°, and dissolves sparingly in cold alcohol and ether, easily in cold, and very easily in hot benzene. When heated with concentrated hydrochloric acid for four hours at 240—250°, it is decomposed into carbonic anhydride, β-naphthol,

and aniline. It is not altered by heating with ammonia or aniline at 270°, or with aqueous potash at 240—250°, and distils almost unchanged at 460°.

Triphenyl-β-naphthylcarbamide, $NPh_2{\cdot}CO{\cdot}NPh{\cdot}C_{10}H_7$, is obtained by heating phenyl-β-naphthylcarbamic chloride with diphenylamine at 200—240° for two hours. It forms a pale-yellow, crystalline powder, melts at 128°, and is easily soluble in cold alcohol and ether, very easily in benzene.

Unsymmetrical diphenyldi-β-naphthylcarbamide, $NPh_2{\cdot}CO{\cdot}N(C_{10}H_7)_2$, is best obtained by heating diphenylcarbamic chloride with β-dinaphthylamine for two hours at 200—220°. It is also obtained by heating di-β-naphthylcarbamic chloride with diphenylamine for three hours at 260°; tetra-β-naphthylcarbamide (m. p. 293—294°) (Kym, *Ber.*, **23**. 1542) being formed at the same time. It melts at 103—104°, and is somewhat easily soluble in cold, easily in hot alcohol and ether or cold benzene, and very easily in hot benzene.

Phenyltri-β-naphthylcarbamide, $N(C_{10}H_7)_2{\cdot}CO{\cdot}NPh{\cdot}C_{10}H_7$, is obtained on heating di-β-naphthylcarbamic chloride with phenyl-β-naphthylamine at 240—260° for three hours. It crystallises from acetic acid in white nodules, melts at 168°, and is sparingly soluble in cold, easily in hot alcohol and ether, and more easily in benzene and acetic acid. At 16°, one part dissolves in 104·5 parts of alcohol, and in 22 parts of benzene.

Carbazole and Carbonyl Chloride.—Various experiments were made with the object of preparing a carbamic chloride by the action of carbonyl chloride on carbazole but without success. Carbonyl chloride is without action on carbazole at 100°, 130°, or 200°, whilst at 250° carbonised products are obtained, together with unaltered carbazole. The potassium derivative of carbazole gives no better results.

E. C. R.

Reduction of Aromatic Aldehydes. By F. Tiemann (*Ber.*, **24**, 3169—3175).—In a former paper, the author has shown (Abstr., 1886, 460) that whilst benzaldehyde readily yields benzyl acetate on treatment with zinc-dust and acetic acid, orthohydroxybenzaldehyde is thus converted into diorthohydroxyhydrobenzoïn diesoanhydride. Further investigation has shown that the reduction of aromatic aldehydes with zinc-dust and acetic acid proceeds differently according to the conditions under which it is carried out; thus parahydroxybenzaldehyde, which usually yields the corresponding alcohol or its acetate, can even be converted into paracresol by long-continued boiling with the reagents. If the reduction proceeds slowly, so that mixtures of the alcohol and aldehyde are subjected for some time to the action of zinc acetate and acetic acid, condensation takes place with formation of substances resembling hydrobenzoïn, according to the equation

$$R{\cdot}CHO + R{\cdot}CH_2{\cdot}OH = R{\cdot}CH(OH){\cdot}CH(OH){\cdot}R.$$

The compound obtained by the author by the reduction of salicylaldehyde, and described as diorthohydroxyhydrobenzoïn diesoanhydride, is in reality a mixture of two isomerides melting at 116—117°

and 67—68° respectively, both of which have probably the constitutional formula $\begin{matrix} C_6H_4\cdot CH\cdot O \\ | \quad\quad | \\ O\text{—}CH\cdot C_6H_4 \end{matrix}$.

Hydrobenzoïn itself contains two asymmetrical carbon atoms, and should therefore exist in three isomeric forms; the anhydride of diorthohydroxyhydrobenzoïn should also, according to theory, form a similar number of isomerides: both of the above compounds are, however, optically inactive, and could not be separated into optically active constituents. The one melting at 67—68° is converted, on boiling in acetic acid solution, into the higher melting isomeride.

If the reduction is carried out quickly, and at as high a temperature as possible, a portion appears to be converted into *diorthohydroxyhydrobenzoïn*, $HO\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot OH$, which, on distillation, splits up into *diorthohydroxystilbene*, $C_2H_2(C_6H_4\cdot OH)_2$, and water.

The experimental details of this research are given in the following abstract. H. G. C.

Reduction of Salicylaldehyde by Zinc-dust and Acetic Acid. By C. D. Harries (*Ber.*, **24**, 3175—3180; see also previous abstract). —In order to prepare the diorthohydroxyhydrobenzoïn diesoanhydride melting at 116—117°, a solution of salicylaldehyde in acetic acid is boiled for 12 hours with an excess of zinc-dust, the solution diluted with water, neutralised with soda, and extracted with ether. After distilling off the ether, the residue is treated with potash, and the insoluble portion recrystallised from alcohol. The anhydride is thus obtained in transparent needles readily soluble in ether and benzene, sparingly in alcohol and acetic acid, and only slightly in hot water; it has a pleasant aromatic odour resembling that of fennel and geranium, dissolves in sulphuric acid with a red coloration, and is not altered by heating with dilute mineral acids or alkalis.

If the action of zinc is allowed to take place at 100°, a mixture of the foregoing compound with an isomeride of lower melting point is formed, which may be separated into its constituents by repeatedly precipitating the alcoholic solution with hot water. The more soluble portion is thus obtained in crystals melting at 67—68°. Both anhydrides appear to distil in a vacuum without decomposition, but the compound of lower melting point is completely converted into its isomeride by boiling in acetic acid solution for some time.

The anhydride of higher melting point is acted on by bromine in acetic acid solution with formation of two *dibromo*-derivatives having the composition $C_{14}H_8O_2Br_2$, which commence to sublime at 235° and 245° respectively.

If the reduction of salicylaldehyde be carried out at 120°, and the product distilled, potash extracts from the distillate *diorthohydroxystilbene*, $C_2H_2\cdot(C_6H_4\cdot OH)_2$, which melts at 95°, is sparingly soluble in water, readily in alcohol and ether, and forms a blue fluorescent solution in alkalis. Its *dibenzoyl* derivative, $C_2H_2(C_6H_4\cdot OBz)_2$, crystallises from alcohol in matted aggregates of needles melting at 107—108°, and unites directly with bromine, forming *dibenzoyldiorthohydroxystilbene dibromide*, $C_{28}H_{20}Br_2O_4$, melting at 58—59°. H. G. C.

Methyl Orthohydroxycinnamyl Ketone (Methyl Orthocumaroketone) and its Derivatives. By C. D. HARRIES (*Ber.*, **24**, 3180—3184).—Tiemann and Kees have shown (Abstr., 1885, 1073) that helicin undergoes condensation with acetone and alkali, forming methyl gluco-orthocumaroketone, which is converted by the action of emulsin into glucose and methyl orthocumaroketone. The latter compound may also be readily obtained by the action of dilute alkali and acetone on salicylaldehyde; the mixture, after remaining for two days, is acidified with hydrochloric acid and freed from unaltered salicylaldehyde by distilling in a current of steam. The insoluble product remaining in the liquid after cooling is recrystallised from benzene with the addition of animal charcoal, and then melts at 139°, as given by Tiemann and Kees. It is readily soluble in alcohol, ether, and hot water, and is coloured bluish-violet by ferric chloride in aqueous solution. When the ketone is dissolved in alcoholic sodium ethoxide and ether added, the *sodium* compound separates in pure condition as a deep yellow substance.

When methyl orthocumaroketone is treated with benzoic chloride in alkaline solution, it yields the *benzoyl* derivative, $C_{10}H_9O_2Bz$, which crystallises from dilute alcohol in white needles melting at 87—88°; the *acetyl* and *methyl* derivatives are oils. The ketone also readily combines with phenylhydrazine and hydroxylamine, forming the *phenylhydrazone*, $C_{10}H_{10}O{:}N_2HPh$, and the *oxime*, $C_{10}H_{10}O{:}N{\cdot}OH$; the former separates in yellow flakes, which, after recrystallisation from dilute alcohol, melt at 159—160°, and the latter forms white crystals melting at 84—85°.

On reduction with sodium amalgam, methyl orthocumaroketone is converted into secondary methylorthocumaryl alcohol,

$$HO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHMe{\cdot}OH,$$

which, after purification, forms compact plates melting at 47—48°. It is readily soluble in alcohol, ether, benzene, and hot water, gradually becomes pink in the air, dissolves in sulphuric acid with a reddish-violet colour, and does not form an anhydride resembling coumarin. Reducing agents appear to have no effect on the ethylene linking in the side chain, nor does the ketone unite directly with bromine.

H. G. C.

Action of Sodium on Ketones and Aldehydes. By E. BECKMANN and T. PAUL (*Annalen*, **266**, 1—28; compare Abstr., 1889, 78).—The authors have made a study of the sodium derivatives of various ketones and of benzaldehyde; their experiments have shown that many of these substances resemble the organo-metallic compounds in being very readily oxidised on exposure to the air, in being immediately decomposed by water, and in combining with carbonic anhydride to form salts of carboxylic acids. The sodium derivatives were prepared by treating a solution of the ketone or aldehyde in pure ether or benzene with excess of sodium, in the form of wire or ribbon, air and moisture being excluded as far as possible; the products were then washed and dried in an atmosphere of pure hydrogen, in an apparatus specially devised for the purpose; in spite of all

precautions, it was found impossible to avoid partial oxidation, and the preparations usually contained a little metallic sodium. When dry carbonic anhydride is passed into ether containing one of these sodium derivatives in solution or in suspension, combination generally takes place, accompanied usually by a change in colour; the compounds produced in this way are extremely hygroscopic, and decompose on exposure to the air.

The sodium derivative of benzophenone (*loc. cit.*) is immediately decomposed by water, yielding benzopinacone (m. p. 184°), benzophenone, and benzhydrol (m. p. 67°), the relative quantities of these three products depending greatly on the conditions of the experiment. It combines with carbonic anhydride under the conditions just stated, being thereby converted into a yellow powder; this substance is decomposed by water, yielding approximately equal quantities of the sodium salt of benzilic acid and benzophenone. These reactions are best explained by assuming that sodiobenzophenone and its carboxyl derivative have the constitutions expressed by the formulæ $CPh_2Na\cdot O\cdot CPh_2\cdot ONa$ and $COONa\cdot CPh_2\cdot O\cdot CPh_2\cdot O\cdot COONa$ respectively; analyses of the two compounds gave results in accordance with these formulæ.

The sodium derivative of phenyl α-naphthyl ketone is a greenish-yellow powder, and is decomposed by water, yielding a yellow oil; this oil is doubtless a mixture of various compounds, and was proved to contain a crystalline substance melting at about 130°, which is most probably phenyl-α-naphthylpinacoline. When phenyl sodio-α-naphthyl ketone is treated with carbonic anhydride, it is converted into a yellow powder, which on decomposition with water yields the sodium salt of phenyl-α-naphthylglycollic acid and phenyl α-naphthyl ketone; it seems probable, therefore, that this carboxy-derivative has a constitution analogous to that of the corresponding benzophenone derivative, a view which is in agreement with the analytical results.

Phenyl-α-naphthylglycollic acid, $C_{18}H_{14}O_3$, can be conveniently prepared from phenyl sodio-α-naphthyl ketone, as it is unnecessary to purify the carboxy-derivative. It crystallises from hot water or dilute alcohol in colourless, well-defined plates or needles, which contain 2 mols. H_2O and melt at 108—115° with elimination of water; it separates from benzene and carbon bisulphide in anhydrous, short prisms melting at 148°.

When acetophenone is treated with sodium, the ethereal solution turns greenish, and then a colourless powder is deposited; if, however, this powder is left in contact with sodium for a long time, it first turns brown and then dark-violet. On decomposing sodacetophenone with water, acetophenonepinacone (m. p. 122·5°), acetophenone, and other compounds are formed. When the sodium derivative is treated with carbonic anhydride, it yields a yellowish substance which is decomposed by water; if the alkaline solution is extracted with ether, the same compounds are obtained as from sodacetophenone, and benzoylacetic acid (m. p. 100°) remains in the aqueous solution. The constitution of these two sodium compounds is probably expressed by the formulæ $ONa\cdot CPhMe\cdot CPh(OH)\cdot CH_2Na$ and $COONa\cdot O\cdot CPhMe\cdot CPh(OH)\cdot CH_2\cdot COONa$ respectively.

The sodium derivative of deoxybenzoïn is very readily soluble in ether, and is best obtained by treating a concentrated solution of the ketone in pure benzene with sodium; it is a very hygroscopic, pale-yellow substance, and is readily decomposed by water, yielding deoxybenzoïn. The benzene mother liquors obtained in the preparation and purification of this sodium derivative contain deoxybenzoïnpinacone (m. p. 213°) and toluylene hydrate (m. p. 62°). On passing carbonic anhydride into an ethereal solution of sodiodeoxybenzoïn, a reddish-yellow substance is precipitated; this compound is decomposed by water, yielding deoxybenzoïn and an acid which could not be isolated, but which is most probably phenylbenzoylacetic acid. When the aqueous solution of the acid formed in this way is quickly separated from the ethereal solution of deoxybenzoïn and then treated with hydroxylamine, a crystalline acid which melts at 159·5°, and which has probably the constitution $\begin{matrix}\mathrm{N}-\\ \|\\ \mathrm{CPh}\end{matrix}>\mathrm{CPh\cdot COOH}$, is obtained. From these reactions, and from the results of analyses of the two sodium derivatives, the authors conclude that they have the constitution COPh·CHNaPh and COPh·CHPh·COONa respectively.

When an ethereal solution of benzile is treated with sodium, there is formed a yellow, flocculent substance which afterwards changes to a deep violet powder; this compound oxidises very energetically on exposure to the air, and is decomposed by water into benzile and benzoïn, but it seems to be unacted on by carbonic anhydride; its constitution is probably expressed by the formula

$$\mathrm{COPh\cdot CPh(ONa)\cdot CPh(ONa)\cdot COPh}.$$

The compound formed by the action of sodium on a benzene solution of benzaldehyde is a dark-green powder, which becomes much lighter in colour when washed and dried; it oxidises very readily on exposure to the air, and when treated with water it gives hydrobenzoïn and a trace of benzoic acid. It combines with carbonic anhydride, yielding a brownish-yellow substance which is quickly decomposed by water with formation of hydrobenzoïn, sodium hydrogen carbonate, and a trace of benzoic acid. The following formulæ, NaO·CHPh·CHPh·ONa and COONa·O·CHPh·CHPh·O·COONa, probably represent the constitutions of these two sodium derivatives.

F. S. K.

Bromination of Bromobenzoic Acids. By A. Claus and A. Hirsch (*Annalen*, **266**, 203—209).—Dibromobenzoic acid [COOH : Br_2 = 1 : 3 : 4] is formed in small quantities by the bromination of benzoic acid, but the reaction is a very complicated one; by the bromination of metabromobenzoic acid at 220—230°, the 3 : 4-dibromo-acid is produced in even smaller quantities, if at all. When benzoic acid is treated with nascent bromine, in very dilute aqueous solution, at a temperature below 70—80°, not inconsiderable quantities of para-bromobenzoic acid are obtained, but dibromo-acids are not produced in any appreciable quantity.

When orthobromobenzoic acid is heated with bromine (1 mol.) and water at 150—160° for 8 to 10 hours, dibromobenzoic acid [COOH : Br_2

= 1 : 2 : 5] is produced; parabromobenzoic acid is not acted on at 180°, but at 200° it is converted into tribromobenzoic acid [COOH : Br_3 = 1 : 3 : 4 : 5], some of the monobromo-acid remaining unchanged.

These experiments show that in benzoic acid substitution is not limited solely to the meta-position relatively to the carboxyl group, but that, under certain conditions, the ortho- and para-hydrogen atoms may also be displaced. F. S. K.

Nitration of Orthochloroparatoluic Acid. By A. Claus and N. Davidsen (*Annalen*, **265**, 341—350).—The following experiments prove that the nitrochlorotoluic acid (m. p. 180°) previously described (Abstr., 1889, 988) has the constitution [COOH : Cl : Me : NO_2 = 1 : 2 : 4 : 5]; the *magnesium* salt of this acid is readily soluble in water, from which it crystallises in large, hexagonal plates containing 8 mols. H_2O.

Nitrochloroparatoluidine [NH_2 : Cl : Me : NO_2 = 1 : 2 : 4 : 5] is best prepared by treating dry chlorotoluidine nitrate with pure sulphuric acid cooled to about −15°; the yield is quantitative. It crystallises from hot alcohol in orange-red plates, melts at 129·5° (uncorr.), and is only sparingly soluble in boiling water and dilute acids, but readily in ether, alcohol, &c. The *acetyl* derivative, $NO_2 \cdot C_6H_2ClMe \cdot NHAc$, crystallises from alcohol in small, almost colourless needles, melts at 143° (uncorr.), and is not decomposed by boiling sulphuric acid; when heated with fuming hydrochloric acid at 150°, it is reconverted into nitrochloroparatoluidine.

Nitrochloroparatoluidine [NH_2 : Cl : Me : NO_2 = 1 : 2 : 4 : 6] is formed when dry chlorotoluidine nitrate is treated with 80 per cent. sulphuric acid cooled to about 0°; it is best obtained by treating chloroparacetotoluidide with nitric acid of sp. gr. 1·5 at about 20°, and then decomposing the product with sulphuric acid. It crystallises from alcohol in orange-coloured plates, melts at 70·5, and is readily volatile with steam. The *acetyl* derivative crystallises in almost colourless needles and prisms melting at 196° (uncorr.).

Nitrochloroparatolunitrile [CN : Cl : Me : NO_2 = 1 : 2 : 4 : 5] is easily obtained from the corresponding amido-derivative; the yield of the pure compound is 70 per cent. of the theoretical. It crystallises from ether or alcohol in long, almost colourless needles melting at 93° (uncorr.); when boiled with sulphuric acid or with very dilute potash, it is converted into the nitrochloroparatoluic acid (m. p. 180—181·5°) referred to above.

Amidochloroparatoluic acid [COOH : Cl : Me : NH_2 = 1 : 2 : 4 : 5], prepared by reducing the corresponding nitro-derivative (m. p. 180—181·5) with tin and hydrochloric acid in alcoholic solution, crystallises from hot water in colourless needles melting at 220° (uncorr.). The *hydrochloride* crystallises in slender, colourless needles, and melts at about 245° with decomposition. The stannochloride is readily soluble in water, and crystallises in colourless needles. When the diazo-derivative of the amido-acid is treated with cuprous chloride, it is converted into dichloroparatoluic acid [COOH : Cl_2 : Me = 1 : 2 : 5 : 4], melting at 187° (uncorr.). The *barium* salt of this acid crystallises from cold water in needles containing 4 mols. H_2O.

Bromochloroparatoluic acid [COOH : Cl : Br : Me = 1 : 2 : 5 : 4], prepared by decomposing the diazo-derivative of the amido-acid with cuprous bromide, is almost insoluble in water, but readily in alcohol, from which it crystallises in colourless, nacreous needles melting at 192—193° (uncorr.). The *barium* salt is readily soluble in water, from which it crystallises in colourless needles containing $1\frac{1}{2}$ mols. H_2O.

Nitrochloroparatoluic acid [COOH : Cl : NO_2 : Me = 1 : 2 : 3 : 4] is formed in small quantities on nitrating orthochloroparatoluic acid, and is best prepared from the isomeride (m. p. 181°) referred to above by means of its *magnesium* salt, with $3\frac{1}{2}H_2O$, which is more soluble in water than that of the isomeric acid. It crystallises from dilute alcohol in colourless needles, melts at 192° (uncorr.), and is insoluble in light petroleum; when treated with a mixture of nitric and sulphuric acids, it is converted into the dinitrochloroparatoluic acid previously described. F. S. K.

Nitration of Metachloroparatoluic Acid. By A. Claus and P. Böcher (*Annalen*, **265**, 351—363).—Three isomeric nitro-derivatives are invariably produced when metachloroparatoluic acid is nitrated under various conditions; 60—70 per cent. of the crude product consists of the acid of the constitution [COOH : Cl : Me : NO_2 = 1 : 3 : 4 : 6], 20—30 per cent. of the corresponding 1 : 3 : 4 : 5-derivative, and 5—10 per cent. of the 1 : 3 : 4 : 2-acid. The three compounds can be separated from one another by systematic fractional crystallisation of the free acids and their barium salts alternately; they are all very readily soluble in acetone, ether, and alcohol, but only sparingly in light petroleum, and very sparingly in benzene.

The 1 : 3 : 4 : 6-acid can also be obtained in a pure condition from nitrochloroparatoluidine in the manner described below.

Nitrochloroparacetotoluide [NHAc : Cl : Me : NO_2 = 1 : 3 : 4 : 6] is prepared by nitrating chloroparacetotoluidide with acid of sp. gr. 1·52; it crystallises from alcohol in lustrous plates and in small needles, both forms melting at 113° (uncorr.).

Nitrochloroparatoluidine [NH_2 : Cl : Me : NO_2 = 1 : 3 : 4 : 6], obtained by decomposing the acetyl derivative with boiling alcoholic potash, crystallises from hot alcohol, in which it is readily soluble, in lustrous, golden plates, melts at 165° (uncorr.), and is only sparingly soluble in hot water; it is readily volatile with steam. The corresponding *nitrile* crystallises in large plates, sublimes without decomposition, melts at 157° (uncorr.), and is readily soluble in alcohol. The corresponding *acid*, obtained by treating the nitrile with concentrated sulphuric acid at about 200°, crystallises from alcohol in colourless needles, melts at 184—185°, and sublimes without decomposition. The *barium* salt, with $1\frac{1}{2}H_2O$, crystallises in large, colourless, hexagonal plates. The *calcium* salt and the bluish-green *copper* salt are anhydrous, but the *potassium* salt crystallises in plates containing $\frac{1}{2}$ mol. H_2O.

Amidochloroparatoluic acid [COOH : Cl : Me : NH_2 = 1 : 3 : 4 : 6] is obtained when the nitro-acid just described is reduced with iron and hydrochloric acid; it crystallises from alcohol in colourless needles, and melts at about 220°. When its diazo-derivative is treated with cuprous chloride, dichloroparatoluic acid (m. p. 187°) is ob-

tained. This fact proves that the nitro-acid has the constitution assigned to it above.

Nitrochloroparatoluic acid [COOH : Cl : Me : NO_2 = 1 : 3 : 4 : 5] is moderately easily soluble in water, from which it crystallises in slender, colourless needles melting at 159° (uncorr.); it is identical with the acid obtained by Claus and Beysen from dilute nitroparatoluic acid, and both compounds yield one and the same dichloroparatoluic acid (m. p. 188°). The *barium* salt crystallises from water, in which it is readily soluble, in short, thick prisms containing 1 mol. H_2O. The *calcium* salt crystallises in colourless, anhydrous needles. The *ammonium* salt and the *potassium* salt are readily soluble in water, but the *silver* salt is insoluble.

Nitrochloroparatoluic acid [COOH : Cl : Me : NO_2 = 1 : 3 : 4 : 2] crystallises from water, in which it is readily soluble, in colourless, nacreous plates, and melts at 211°. The *barium* salt, with $1\frac{1}{2}H_2O$, crystallises in characteristic stellate forms. The *calcium* salt crystallises in lustrous, anhydrous needles. F. S. K.

Nitration and Bromination of Orthobromoparatoluic Acid. By A. Claus and J. Herbabny (*Annalen*, **265**, 364—378).—When orthobromoparatoluic acid is treated with nitric acid, two isomeric nitro-derivatives are obtained; the compounds are most easily separated by means of their magnesium salts.

The *nitrobromoparatoluic acid* of the constitution

[COOH : Br : Me : NO_2 = 1 : 2 : 4 : 5]

is formed in by far the larger quantity; it crystallises from alcohol in colourless, nacreous plates, melts at 203° (uncorr.), and is very readily soluble in ether, and moderately easily in hot benzene, but only sparingly in hot water. The *sodium* salt, with $4\frac{1}{2}H_2O$, crystallises in large, efflorescent plates, and is readily soluble in water and alcohol. The *potassium* salt, with $1H_2O$, and the *barium* salt, with $5H_2O$, crystallise in needles; the calcium salt, with $5H_2O$, forms large, efflorescent plates or prisms. The *magnesium* salt, with $7\frac{1}{2}H_2O$, crystallises in lustrous plates. The *chloride*, $NO_2{\cdot}C_6H_2BrMe{\cdot}COCl$, crystallises from light petroleum in colourless plates, melts at 60° (uncorr.), and is readily soluble in chloroform. The *amide*, $NO_2{\cdot}C_6H_2BrMe{\cdot}CO{\cdot}NH_2$, crystallises in colourless needles, melts at 191° (uncorr.), and is readily soluble in alcohol, but more sparingly in water. The *ethyl* salt, $NO_2{\cdot}C_6H_2BrMe{\cdot}COOEt$, melts at 61° (uncorr.), and crystallises from alcohol in colourless, lustrous needles. When the acid is oxidised with potassium permanganate, it yields a bromomonitroterephthalic acid; this compound crystallises from hot water in colourless needles, which seem to melt at 260—261°.

Nitrobromoparatoluidine [NH_2 : Br : Me : NO_2 = 1 : 2 : 4 : 5] is easily obtained by dissolving orthobromotoluidine nitrate in sulphuric acid cooled to 0°; it crystallises from glacial acetic acid or alcohol in pale-yellow needles, melting at 121° (uncorr.). The corresponding *nitrile* [CN : Br : Me : NO_2 = 1 : 2 : 4 : 5] melts at 132° (uncorr.), and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in hot water; when boiled with moderately concentrated sulphuric acid, it is converted into the nitrobromoparatoluic acid (m. p. 203°) described above.

Nitrobromoparatoluic acid [COOH : Br : NO_2 : Me = 1 : 2 : 3 : 4] is only formed in small quantities (6—8 per cent.) in nitrating orthobromoparatoluic acid; it crystallises from alcohol and hot water in slender, colourless needles, melts at 214° (uncorr.), and sublimes in slender needles. The *magnesium* salt, with $3\frac{1}{2}H_2O$, crystallises in colourless plates, and is more readily soluble in water than the corresponding salt of the isomeric acid described above. The *barium* salt, with $4H_2O$, crystallises in large rhombic plates.

Nitrobromoparatoluonitrile [CN : Br : Me : NO_2 = 1 : 2 : 4 : 6] can be prepared by diazotising nitrobromotoluidine (m. p. 64°) in ice-cold 70—80 per cent. sulphuric acid solution, and immediately adding a solution of copper sulphate and potassium cyanide; it crystallises from alcohol in yellowish needles, melts at 130° (uncorr.), and is very sparingly soluble in hot water, but readily in benzene, ether, and chloroform.

Nitrobromoparatoluamide [$CO{\cdot}NH_2$: Br : Me : NO_2 = 1 : 2 : 4 : 6] is formed when the preceding compound is boiled with dilute (1 : 1) sulphuric acid for 8—10 hours; it crystallises from boiling water in colourless needles, melts at 171° (uncorr.), and is readily soluble in alcohol, ether, benzene, and chloroform.

Nitrobromoparatoluic acid [COOH : Br : Me : NO_2 = 1 : 2 : 4 : 6] is obtained in small quantities when the corresponding amide is heated at 220—230° with 20—25 per cent. hydrochloric acid; it crystallises from boiling water in small, colourless needles, melts at 206°, and is very readily soluble in ether, alcohol, chloroform, &c.

When orthobromoparatoluic acid is heated with bromine and water at 90—95° for 4—5 hours, the sole product is a dibromoparatoluic acid, [COOH : Br_2 : Me = 1 : 3 : 6 : 4] melting at 199° (uncorr.), which has been previously prepared by Schultz and Fileti. The *sodium* salt of this dibromo-acid crystallises in large plates containing 7 mols. H_2O. The *chloride*, $C_6H_2Br_2Me{\cdot}COCl$, forms colourless, lustrous needles, and melts at 60°.

Dibromoparatoluic acid [COOH : Br_2 : Me = 1 : 2 : 3 : 4] was obtained in small quantities from the corresponding nitrobromoparatoluic acid; it forms colourless crystals, and seems to melt at 194°.

Dibromoparacetotoluidide [NHAc : Br_2 : Me = 1 : 2 : 6 : 4], can be prepared by heating dibromoparatoluidine (m. p. 73°) with acetic chloride at 100°; it crystallises in long, colourless needles, melts at 183° (uncorr.), and is reconverted into dibromoparatoluidine by boiling alcoholic potash.

Dibromoparatoluonitrile [CN : Br_2 : Me = 1 : 2 : 6 : 4], prepared from dibromoparatoluidine, crystallises in long, colourless needles, melts at 156° (uncorr.), sublimes in needles, and is readily volatile with steam; it is insoluble in water, but dissolves freely in alcohol, ether, benzene, and chloroform. When boiled with 50 per cent. sulphuric acid, it is converted into the corresponding *amide;* this compound crystallises from boiling water in small, colourless plates melting at 148° (uncorr.), and is readily soluble in alcohol, ether, and chloroform.

Dibromoparatoluic acid [COOH : Br_2 : Me = 1 : 2 : 6 : 4] is obtained when the amide just described is heated with concentrated sulphuric acid at 240°; it crystallises and sublimes in colourless needles, melts at 182° (uncorr.), and is only sparingly soluble in hot water, but dissolves freely in ether, alcohol, and chloroform. F. S. K.

Dibromoparatoluic Acid. By A. Claus and R. Seibert (*Annalen*, **265**, 378—380).—*Dibromoparatoluonitrile* [CN : Br_2 : Me = 1 : 3 : 5 : 4], prepared from the corresponding dibromotoluidine, crystallises from alcohol in lustrous needles melting at 49° (uncorr.); it is readily volatile with steam, and dissolves freely in alcohol, ether, chloroform, and hot water. The corresponding *acid* is obtained when the nitrile is boiled with potash; it crystallises from alcohol in slender needles, melts at 235—236° (uncorr.), and is readily soluble in alcohol, ether, and chloroform, but only sparingly in water. The *sodium* salt, with $1H_2O$, *potassium* salt, with $1\frac{1}{2}H_2O$, and the *barium* salt, with $4H_2O$, are colourless, crystalline compounds. The *chloride*, $C_6H_2Br_2Me{\cdot}COCl$, crystallises from ether in colourless needles melting at 80° (uncorr.). The *amide* separates from ether in small needles, and melts at 117° (uncorr.). The *ethyl* salt, $C_6H_2Br_2Me{\cdot}COOEt$, crystallises from alcohol in colourless needles melting at 79—80° (uncorr.). F. S. K.

Nitration of Orthonitroparatoluic Acid. By A. Claus and J. Joachim (*Annalen*, **266**, 209—222; compare Rozanski, Abstr., 1890, 52).—Two dinitro-compounds are formed when orthonitroparatoluic acid (m. p. 164°) is heated at about 100° for 4—5 hours with a mixture of nitric and sulphuric acids; the two products are separated by fractional crystallisation from water.

The dinitroparatoluic acid of the constitution [COOH : $(NO_2)_2$: Me = 1 : 2 : 3 : 4] is always produced in by far the smaller quantity, and is much more sparingly soluble in water than the isomeride described below; it crystallises in short, colourless, lustrous prisms, melts at 248° (uncorr.), has an intensely bitter taste, and is readily soluble in alcohol. The barium salt, with $3H_2O$, and the calcium salt, with $1\frac{1}{2}H_2O$, are colourless, crystalline compounds, only moderately easily soluble in water.

Diamidoparatoluic acid [$(NH_2)_2$ = 2 : 3], prepared by reducing the preceding compound with tin and hydrochloric acid, crystallises in yellowish needles, melts at 192°, decomposes at a higher temperature, and is only sparingly soluble in cold water, but readily in alcohol and hot water; in its aqueous solution, ferric chloride produces a red, flocculent precipitate, and its solutions in acids yield with rhodizonic acid a brown azine, which dissolves in alkalis with a violet coloration. The *hydrochloride*, $C_8H_{10}N_2O_2$,2HCl, forms granular crystals, which soon assume a reddish hue. The *barium* salt is moderately easily soluble in water, and crystallises in small, reddish-yellow plates.

Dinitroparatoluic acid [COOH : $(NO_2)_2$: Me = 1 : 2 : 5 : 4] is the principal product of the nitration of paratoluic acid; it is readily soluble in alcohol, and moderately easily in hot water, crystallising in colourless plates which melt at 194°. The *barium* salt, with $2H_2O$, and the *calcium* salt, with $2H_2O$, are colourless, crystalline compounds, only moderately easily soluble in water. The corresponding *diamido*-compound crystallises from boiling water in lustrous, blue or violet needles, melts at 240° (uncorr.) with decomposition, and is very readily soluble in alcohol; when heated with ferric chloride in aqueous solution,

a reddish-brown precipitate is formed, and a strong odour of toluquinone is observed. The *hydrochloride* forms brownish-red crystals.

Dinitroparatoluic acid [COOH : $(NO_2)_2$: Me = 1 : 3 : 5 : 4] is the sole product of the nitration of metanitroparatoluic acid; it melts at 159° (uncorr.). The barium salt and the calcium salt contain water of crystallisation. The corresponding *diamido*-acid crystallises from water in light grey needles, melts at 212° (uncorr.) without decomposition when quickly heated, and is readily soluble in alcohol; its aqueous solution, even when very dilute, gives an intense yellow coloration with nitrous acid. The *barium* salt crystallises in anhydrous, light grey plates. F. S. K.

Dinitroparatoluic Acids and their Derivatives. By A. Claus and C. Beysen (*Annalen*, **266**, 223—239).—*Dinitroparatoluonitrile* [CN : $(NO_2)_2$: Me = 1 : 2 : 6 : 4] can be obtained by adding sodium nitrite in small portions at a time to a well-cooled sulphuric acid solution of 2 : 6-dinitroparatoluidine and, after keeping for a short time, pouring the mixture drop by drop into ice-cold water; the solution is filtered from unchanged dinitroparatoluidine, mixed in the cold with a solution of copper cyanide, and then warmed on the water-bath to complete the reaction. It crystallises from alcohol in golden needles, melts at 103° (uncorr.), and is readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid, but only sparingly in hot water. The corresponding *amide*, prepared by boiling the nitrile with moderately concentrated sulphuric acid, crystallises in yellow needles, melts at 255—257° (uncorr.), and is readily soluble in alcohol, ether, chloroform, and hot water.

Dinitroparatoluic acid [$(NO_2)_2$ = 2 : 6] is formed when the amide just described is heated at 220—230° for 8 hours with concentrated hydrochloric acid; it crystallises from boiling water in almost colourless plates or prisms, melts at 226° (uncorr.), sublimes in needles, and has an intensely bitter taste; it dissolves freely in alcohol, ether, benzene, chloroform, glacial acetic acid, and hot water, but is only sparingly soluble in cold water. The *barium* salt, with $1H_2O$, crystallises in yellow prisms, and is very readily soluble in hot water.

Azimidoparatoluic acid, $^{1}COOH\cdot C_6H_2{}^{4}Me<{}^{2}_{3}NH_{N}>N$, is formed when the hydrochloride of the 2 : 3-diamido-acid already described (compare preceding abstract) is treated with sodium nitrite in aqueous solution; it crystallises from hot water or alcohol in colourless, lustrous needles, melts at 295° (uncorr.) with decomposition, and is readily soluble in ether and chloroform. The *barium* salt, with $3H_2O$, and the *calcium* salt, with $2H_2O$, crystallise in colourless needles, and are very readily soluble in hot water.

When the diamido-compound, obtained from the 2 : 5-dinitrotoluic acid (*loc. cit.*), is diazotised and the product treated with cuprous bromide, it is converted into dibromoparatoluic acid [COOH : Br_2 : Me = 1 : 2 : 5 : 4].

Nitramidoparatoluic acid [COOH : NO_2 : Me : NH_2 = 1 : 2 : 4 : 5] is

obtained when a solution of the 2:5-dinitro-acid in warm, concentrated ammonia is treated with hydrogen sulphide; it crystallises from boiling water in long, yellow prisms and needles, melts at 220° with decomposition, and is readily soluble in alcohol, ether, and hot water. The *barium* salt crystallises in yellowish-brown plates or prisms, and is anhydrous.

Nitrobromoparatoluic acid [COOH : NO_2 : Me : Br = 1 : 2 : 4 : 5], prepared by decomposing the diazo-derivative of the preceding compound with cuprous bromide, crystallises in colourless needles, melts at 181° (uncorr.) and is readily soluble in hot water, alcohol, ether, and chloroform, but almost insoluble in cold water. The corresponding chloro-derivative, obtained in like manner, melts at 184° (uncorr.), and is identical with the metachloroparatoluic acid previously described by Claus and Böcher (this vol., p. 173).

Nitramidoparatoluic acid [COOH : NO_2 : Me : NH_2 = 1 : 3 : 4 : 5], obtained by reducing the corresponding dinitro-compound (see preceding abstract) with ammonium sulphide, or with the theoretical quantity of stannous chloride in alcoholic hydrochloric acid solution, crystallises from water in lemon-yellow, lustrous needles, melts at 214° (uncorr.), and sublimes without decomposition; it is only sparingly soluble in cold water, but readily in alcohol, ether, and hot water. The *barium* salt, with $4H_2O$, *calcium* salt (anhydrous), *sodium* salt, with $\frac{3}{4}H_2O$, and the *magnesium* salt, with $5H_2O$, are yellow, crystalline compounds. The *nitrobromo*-acid [COOH : NO_2 : Me : Br = 1 : 3 : 4 : 5], prepared by decomposing the diazo-derivative of the amido-acid with cuprous bromide, crystallises from dilute alcohol in small, colourless needles, melts at 181° (uncorr.), and is readily soluble in ether, alcohol, and chloroform, but only sparingly in boiling water; its *barium* salt crystallises from boiling water, in which it is readily soluble, in compact needles. The corresponding nitrochloro-acid, prepared in like manner, melts at 158°, and is identical with the acid obtained by Claus and Böcher (*loc. cit.*) by nitrating metachloroparatoluic acid.

Dichloroparatoluic acid [COOH : Cl_2 : Me = 1 : 3 : 5 : 4] was prepared from the diamido-acid (m. p. 212°) described in the preceding abstract; it was found to be identical with the compound obtained from chloronitrotoluic acid (m. p. 159°) by Claus and Böcher (*loc. cit.*).

F. S. K.

Derivatives of Ethyl Dinitrophenylacetate. By M. Dittrich and V. Meyer (*Annalen*, **266**, 29—30).—Claus has pointed out that some of the compounds lately described by the authors (Abstr., 1891, 1224) were prepared by him a short time ago (Abstr., 1890, 979); the authors acknowledge Claus' claim to priority. F. S. K.

Diphenylmaleïc Anhydride. By S. Gabriel and G. Cohn (*Ber.*, **24**, 3228—3230).—From the constitutional formulæ of maleïc anhydride and phthalic anhydride, it seems probable that both compounds would show similar reactions, and observations have already been made which confirm this supposition; thus both yield ketonic acids with aromatic hydrocarbons, as, for example,

$$COPh{\cdot}CH{:}CH{\cdot}COOH \text{ and } COPh{\cdot}C_6H_4{\cdot}COOH;$$

and both are converted into fluoresceïns by the action of resorcinol (Abstr., 1882, 1074; 1884, 1340).

The authors have further examined the behaviour of diphenylmaleïc anhydride towards phenylacetic acid, and find that it acts in a similar manner to phthalic anhydride, forming a substance closely resembling benzalphthalide (Abstr., 1878, 734; 1886, 265). The diphenylmaleïc anhydride was prepared according to the method given by Reimer (Abstr., 1881, 169), and was heated with phenylacetic acid and sodium acetate at 190°, the temperature being raised to 220—225° as soon as the reaction had moderated. The product is powdered, freed from impurities by extraction with alcohol, and recrystallised from acetic acid, when it is obtained in yellowish needles, having the composition $C_{23}H_{16}O_2$; it is sparingly soluble in alcohol, readily in acetic acid and acetone, and very easily in chloroform and boiling benzene. It is formed according to the equation

$$\begin{matrix}\mathrm{CPh{\cdot}CO}\\ \|\\ \mathrm{CPh{\cdot}CO}\end{matrix}\!\!>\!O + CH_2Ph{\cdot}COOH = \begin{matrix}\mathrm{CPh{\cdot}C(CHPh)}\\ \|\\ \mathrm{CPh\text{———}CO}\end{matrix}\!\!>\!O + CO_2 + H_2O.$$

and may, therefore, be termed *benzaldiphenylmaleïde*. In all its reactions, it closely resembles benzalphthalide.

Diphenylmaleïc anhydride also combines with phenol, resorcinol, and dimethylmetamidophenol forming coloured compounds, and with quinaldine yields a colouring matter resembling quinophthalone. All these substances are being further investigated. H. G. C.

Composition and Crystalline Form of Barium Isophthalate. By W. Lossen and C. Rahnenführer (*Annalen*, **266**, 30—33).—When a solution of barium isophthalate evaporates at the ordinary temperature, well-defined, triclinic crystals of the composition $C_8H_4O_4Ba + 6H_2O$, are deposited; these crystals rapidly effloresce when kept over sulphuric acid, but only slowly in the air. The authors' experiments point to the non-existence of the salts containing 3 and $3\frac{1}{2}$ mols. H_2O, which have been described by Fittig and Velguth and by Kelbe respectively. F. S. K.

Opianic Acid. By G. Goldschmiedt (*Monatsh.*, **12**, 474—478).—When a solution of opianic acid (10 grams) and acetone (6 grams) in water (750 grams) is treated with a 10 per cent. solution of sodium hydroxide (30 c.c.), and allowed to remain for 24 hours at the ordinary temperature, condensation takes place with formation of the compounds $C_{23}H_{22}O_9$ and $C_{13}H_{14}O_5$. The former crystallises from alcohol, in which it is but sparingly soluble, in felted needles, does not dissolve in cold solutions of the alkali carbonates, is not changed by bromine in ethereal solution, and melts at 151°. The latter, which is the chief product of the reaction, crystallises from dilute alcohol in white needles, melts at 117°, and resembles the former compound in its behaviour towards bromine and the alkalis.

Under like conditions, opianic acid and acetophenone give the compound $C_{18}H_{16}O_5$, which crystallises from alcohol in beautiful,

glistening plates, and melts at 127—128°. It also is unacted on by bromine and by cold solutions of the alkalis.

The three new compounds above described are not acids, nor do they contain doubly-linked carbon atoms. Their constitution is probably to be regarded as $CO[CH_2{\cdot}CH<^{C_6H_2(OMe)_2}_{O\text{———}}>CO]_2$, $CO\text{———}O$ / $C_6H_2(OMe)_2$ $>CH{\cdot}CH_2{\cdot}COMe$, and $CO\text{———}O$ / $C_6H_2(OMe)_2$ $>CH{\cdot}CH_2{\cdot}COPh$, respectively. It is obvious in this case that opianic acid does not behave as an aldehydic acid; for if it did, feeble, unsaturated acids of the formulæ $CO[CH{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}COOH]_2$,

$COOH{\cdot}C_6H_2(OMe)_2{\cdot}CH{:}CH{\cdot}COMe$, and

$COOH{\cdot}C_6H_2(OMe)_2{\cdot}CH{:}CH{\cdot}COPh$,

respectively, would result from the condensation with acetone and benzophenone (compare Goldschmiedt and Egger, Abstr., 1891, 1371).

G. T. M.

Oximes of Opianic and Phthalaldehydic Acids. By O. Allendorff (*Ber.*, **24**, 3264—3266).—In a recent paper (Abstr., 1891, 1369), the author stated that the oxime of opianic acid was not known, he having at the time overlooked its description by W. H. Perkin, jun. (Trans., 1890, 1069). A. R. L.

Metahemipinic Acid. By O. Rossin (*Monatsh.*, **12**, 486—500; compare Goldschmiedt, Abstr., 1889, 167).—This acid has the constitution $C_6H_2(OMe)_2(COOH)_2$ [= 1 : 2 : 4 : 5], and forms an *ethyl hydrogen* salt which melts at 127°, and a *diethyl salt* which is an uncrystallisable syrup, and can be distilled unchanged under a reduced pressure of 160 mm. The acid is converted by concentrated nitric acid into *dinitroveratroïl*, $C_8H_8O_6N_2$, which crystallises from dilute alcohol in pale-yellow needles, melts at 131—132°, is only slightly soluble in water, and appears to be identical with Merck's dinitroveratroïl (*Annalen*, **108**, 60). On heating the acid with hydriodic or hydrochloric acid, *normetahemipinic acid*, $C_8H_6O_6$ [$(OH)_2 : (COOH)_2$ = 1 : 2 : 4 : 5], was obtained. It crystallises with 1 mol. H_2O, which is not expelled on heating at 100° under the ordinary pressure, and is only slowly given up at that temperature in a vacuum. This acid is readily soluble in alcohol, dissolves sparingly in ether, crystallises from water in rhombic prisms [$a : b : c$ = 1 : 0·08837 : 0·5879], and from acetone in beautiful needles. At 180° it gives a trace of a yellow sublimate, which increases in quantity and turns red on further heating, whilst at 247·5° it melts, having been converted into normetahemipinic anhydride.

The *ethyl hydrogen* salt of norhemipinic acid, $C_{10}H_{10}O_6$, is obtained on heating normetahemipinic anhydride and absolute alcohol in a reflux apparatus for three hours. It crystallises from alcohol and ether in needles, which, if quickly heated, melt at 182°, but, if heated more gradually, melt at 175°. The *diethyl* salt, $C_{12}H_{14}O_6$, crystallises in

small needles which melt at 148·5—149·5°, and is readily soluble in alcohol. With ferric chloride, both the acid and its ethyl salts give an emerald-green coloration, which is characteristic of substances derived from protocatechuic acid. G. T. M.

Derivatives of Tannin. By C. Böttinger (*Arch. Pharm.*, **229**, 439—447; compare Abstr., 1890, 1275).—*Ethyl ditannacetoacetate*, $C_{34}H_{32}O_{22}$, is prepared by heating a mixture of tannin (20 grams) and potassium hydrogen sulphate (30 grams) with ethyl acetoacetate (30 grams) at 190—200° for 15 minutes, and then adding more ethyl acetoacetate (10 c.c.), and heating for another five minutes. The melt is extracted with water and ether, whereby the larger quantity of the ethyl ditannacetoacetate is left as a semi-solid mass, which is dried in a desiccator.

Ethyl ditannacetoacetate is a yellowish powder, which dissolves freely in alcohol, ethyl acetate, and ethyl acetoacetate, but very little in cold water; in hot water it is somewhat soluble, but is decomposed thereby, for, on cooling, slender, felted needles separate, which differ from the original compound in containing 1 mol. less of water. When boiled with water, ethyl ditannacetoacetate is decomposed with evolution of acetone; when heated in a sealed tube with water at 160°, acetone, carbonic anhydride, gallic acid, and tannin can be recognised as decomposition products. Several minor reactions are given in the paper.

Ethyl tannacetoacetate, $C_{20}H_{20}O_{12}$, is formed when the heating, in the process for preparing the di-derivative, is continued for 40 minutes. The melt is extracted as described above, and the residue dissolved in alcohol, mixed with ether, filtered, and evaporated at a gentle heat. The semi-liquid residue is poured into cold water, when the ethyl tannacetoacetate is separated; it is dried in a desiccator. Ethyl tannacetoacetate behaves with solvents similarly to the di-derivative, but does not dissolve in hot water more than in cold. When heated with water at 160°, it behaves like the di-derivative.

Hydrotannic and isohydrotannic acids are obtained when tannin (20 grams) is mixed with potassium hydrogen sulphate (30 grams) and glycerol (30 grams), and heated at 190—200° for 54 minutes. The melt is extracted with water and the residue dried and extracted with absolute alcohol; this extract is evaporated and the semi-liquid residue is treated with much alcohol and ether; the isohydrotannic acid is thus precipitated, whilst the hydrotannic acid remains in solution, and is precipitated by pouring the solution into water.

The *hydrotannic acid*, $C_{14}H_{14}O_7 + H_2O$, is purified by dissolving it in acetic acid and precipitating it again by the addition of water and a few drops of hydrochloric acid. It is a brown powder, which dissolves easily in cold alcohol, dilute acetic acid, and warm acetic anhydride, but not in water; when heated with zinc-dust, it gives the same sharp odour which was noticed with hydroquercic acid (Abstr., 1891, 1061). It dissolves in ammonia with a brown colour; the solution absorbs oxygen, and is reprecipitated by acetic and hydrochloric acids. It yields a yellow *acetyl* derivative, $C_{14}H_{10}Ac_4O_7$, when heated with acetic anhydride at 100°.

Isohydrotannic acid, $C_{14}H_{14}O_7$, is insoluble in cold water and absolute alcohol, but dissolves slightly in hot water, and easily in hot, aqueous alcohol; it behaves similarly to hydrotannic acid, and yields a brown *acetyl* derivative, which is probably $C_{14}H_{11}Ac_3O_7$.

The author concludes that these acids have high molecular weights, are not glycerides, and contain no glycerol residue. A. G. B.

1:2:4-Chloronitrobenzenesulphonic Acid and 1:4:2-Chloronitrobenzenesulphonic Acid. By P. Fischer (*Ber.*, **24**, 3185—3197).—Of the ten possible chloronitrobenzenesulphonic acids, only three have hitherto been prepared, and the exact constitution of these is known in only one case, namely, that of the 1:4:3-chloronitrobenzenesulphonic acid (Abstr., 1882, 593). The remaining two were prepared by Post and Meyer (Abstr., 1881, 1037), and were also obtained by Allert (Abstr., 1881, 902) who regarded them as a single acid; the latter further erroneously supposed that the chlorine occupied the adjacent position to the sulphonic acid group, and his conclusions are therefore incorrect.

1:2:4-*Chloronitrobenzenesulphonic acid*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_3H$, may be obtained either by the sulphonation of orthochloronitrobenzene or by the nitration of parachlorobenzenesulphonic acid; the latter method gives the best results, as commercial orthochloronitrobenzene contains large quantities of the para-compound. To prepare the sulphonic acid, 100 grams of chlorobenzene is treated with a mixture of 140 grams of crystallised pyrosulphuric acid and 140 grams of concentrated sulphuric acid, and the whole warmed for some time on the water-bath to convert into the sulphonic acid a small quantity of paradichlorodiphenylsulphone, which is always simultaneously formed; the nitration is carried out by adding 280 grams of barium nitrate, after which the whole is treated with a little water and the nitrous fumes removed by passing a strong current of air through the liquid. The acid is isolated as the barium salt, the latter being decomposed with sulphuric acid; it separates from a concentrated aqueous solution in slender, deliquescent needles, is soluble in alcohol, acetone, and acetic acid, insoluble in ether and benzene, and has a pleasant, aromatic odour and bitter, astringent taste. The *barium* salt, $(NO_2{\cdot}C_6H_3Cl{\cdot}SO_3)_2Ba + H_2O$, forms compact, yellow crystals or pale-yellow, lustrous plates; the *ammonium* salt, colourless, anhydrous needles; and the *copper* salt, emerald-green needles. The *sulphochloride*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_2Cl$, crystallises from ether in large, transparent crystals melting at 40—41°, and the *sulphonamide*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}SO_2NH_2,$$

separates from water in pale-yellow prisms, and from alcohol in yellowish-white needles melting at 175—176°.

When the above sulphonic acid is reduced with ferrous sulphate and baryta-water, according to Claisen and Thompson's method (*Ber.*, **12**, 1946; **13**, 2126), it yields the *barium* salt of 1:2:4-*chloramidobenzenesulphonic acid*, $(NH_2{\cdot}C_6H_3Cl{\cdot}SO_3)_2Ba + 4H_2O$, which crystallises in colourless needles and only loses the last mol. of water of crystallisation at 210—215°. The *potassium* salt forms colourless,

anhydrous needles or plates. The free acid is obtained from the barium salt by exact precipitation with sulphuric acid, and separates from the solution in long, lustrous, white needles, the aqueous solution of which is coloured dark brown by ferric chloride.

1 : 4 : 2-*Chloronitrobenzenesulphonic acid* is obtained by heating 1 part of parachloronitrobenzene with a mixture of 4 parts of crystallised pyrosulphuric acid and 2 parts of concentrated sulphuric acid in a sealed tube at 120—130°, and is isolated as usual by means of the barium salt. It crystallises in beautiful, long needles or large, transparent crystals containing 2 mols. H_2O, and is not hygroscopic. The *barium* salt forms colourless, lustrous, anhydrous plates; the *potassium* salt, lustrous, white needles; the *sulphochloride*, beautiful, transparent crystals melting at 89—90°; and the *sulphonamide*, lustrous, white plates or small, colourless needles.

1 : 4 : 2-Chloronitrobenzenesulphonic acid is also readily reduced by ferrous sulphate and baryta-water with formation of 1 : 4 : 2-*chloramidobenzenesulphonic acid*, $NH_2{\cdot}C_6H_3Cl{\cdot}SO_3H$, which is obtained from the barium salt by the action of sulphuric acid, and crystallises in anhydrous, lustrous, white needles; the *barium* salt with $4H_2O$, forms colourless needles. H. G. C.

Note by Abstractor.—1 : 4 : 2-Chloronitrobenzenesulphonic acid has also been recently described by Claus and Mann (Abstr., 1891, 1488), together with all its above-mentioned derivatives. Both descriptions agree well together, except in the case of the barium salt of 1 : 4 : 2-chloroamidobenzenesulphonic acid, which, according to Claus and Mann, contains $6H_2O$ instead of $4H_2O$, as given by Fischer. H. G. C.

Diphenylenazone. By E. Täuber (*Ber.*, **24**, 3081—3088; compare Abstr., 1891, 570).—*Diphenylenazone dioxide*, $\begin{matrix}NO{\cdot}C_6H_4\\ \|\ \ |\\ NO{\cdot}C_6H_4\end{matrix}$ [NO : NO = 3 : 6′], is prepared by dissolving orthodinitrodiphenyl (*loc. cit.*) (5 grams) in boiling 90 per cent. alcohol (100 c.c.), adding 40 per cent. aqueous potash (3 c.c.), and then zinc-dust (15 grams) in successive small portions, and finally boiling for half an hour in a reflux apparatus and filtering the solution. The yield is about 25 per cent. of the theoretical. The substance crystallises from alcohol in needles or in lustrous plates very faintly tinged with yellow. It melts with decomposition at 240°, explodes when heated, and is reduced to the azone by sodium amalgam. It is insoluble in water, dissolves very slightly in concentrated hydrochloric acid, light petroleum, and cold alcohol, sparingly in ether and cold acetic acid, rather sparingly in boiling alcohol, benzene, and toluene, easily in hot acetic acid, very easily in chloroform and phenol.

Diphenyleneazonemonoxide, $O<\begin{matrix}N{\cdot}C_6H_4\\ \|\ \ |\\ N{\cdot}C_6H_4\end{matrix}$ [N_2O = 6 : 6′], is obtained from the mother liquor of the dioxide, and is separated from the latter substance by a long and tedious process of recrystallisation from alcohol and fractional precipitation from a solution in hydrochloric acid by the addition of water. It can also be obtained by

reducing orthodinitrodiphenyl with sodium amalgam. It crystallises from dilute alcohol in long, pale-yellow needles, with a silky lustre, melts at 152°, dissolves very readily in chloroform, readily in alcohol, boiling benzene, toluene, and acetic acid, sparingly in hot water, very sparingly in cold water and ether, and not at all in light petroleum. It dissolves readily in concentrated, sparingly in dilute, acids; the solvents have a deep-yellow colour. By sodium amalgam, it is reduced to the azone.

Diphenylenazone, $C_{12}H_8N_2$ [N : N = 6 : 6′], is obtained by dissolving orthodinitrodiphenyl (5 grams) in methyl alcohol (200 c.c.), adding, gradually, 3 per cent. sodium amalgam (250 grams) to the cooled solution, filtering, concentrating to a small bulk, and adding water. The substance is dissolved in hydrochloric acid and precipitated with ammonia, and then recrystallised from dilute alcohol. The yield was 2 grams. It melts at 156°, and boils above 360°, almost without decomposition. It crystallises with great readiness; especially fine crystals are obtained from a solution in benzene. It is pale greenish-yellow in colour, and gives, with acids, yellow solutions, from which, however, no salts can be isolated. It dissolves very readily in chloroform and acetic acid, readily in alcohol, benzene, and toluene, sparingly in ether and light petroleum, and not at all in water. When reduced with zinc-dust and hydrochloric acid, it yields *diphenylenehydrazone*, $C_{12}H_8{\cdot}N_2H_2$ [NH : NH = 6 : 6′], the *hydrochloride* of which, $C_{12}H_{10}N_2,HCl$, forms white needles insoluble in 20 per cent. hydrochloric acid. The salt, and still more so the base itself, is very unstable, oxidising in the air to the azone. It is unaffected by reducing agents.

Diamidodiphenyleneazone, $\begin{matrix} N{\cdot}C_6H_3{\cdot}NH_2 \\ \| \quad | \\ N{\cdot}C_6H_3{\cdot}NH_2 \end{matrix}$ [NH_2 : N = 4 : 6 and 4′ : 6′], is prepared by reducing a solution of metadinitrobenzidine in methyl alcohol with sodium amalgam. The residue left after evaporating the alcohol is dissolved in dilute acetic acid, reprecipitated with ammonia, and crystallised from very dilute alcohol. It forms small, dark-red prisms, $C_{12}H_{10}N_4 + 2H_2O$, which lose 1 mol. H_2O over sulphuric acid, and the second at 100°. The anhydrous substance begins to decompose at 260° and melts at 267°. It dissolves readily in alcohol, sparingly in chloroform, toluene, benzene, and ether, very sparingly in water, and not at all in light petroleum. When dissolved in a small quantity of hydrochloric acid, it combines with 2 mols. HCl and forms a greenish-grey solution; on adding more acid, it combines with a third molecule of hydrogen chloride, and the colour changes to reddish-violet. It is a basic dye, and colours tanned cotton greenish-grey. C. F. B.

Stilbene, Thionessal, and Tolallyl Sulphide (Tolane Sulphide).—By E. Baumann and M. Klett (*Ber.*, **24**, 3307—3314.)—When the polymeric thiobenzaldehyde which melts at 83—90°, $(C_6H_5{\cdot}CHS)_n$, n = 10 or 12, is heated at 150°, it is decomposed into sulphur and stilbene, CHPh:CHPh, and at 190° the reaction takes place more readily. But if the temperature rises above 200°, some

hydrogen sulphide is evolved and thionessal formed. The two trithiobenzaldehydes melting at 167° and 225° respectively behave in a similar manner, except that the latter is not attacked until heated above its melting point, when some thionessal is also formed.

There was little doubt that the thionessal mentioned above was formed by a secondary action of the sulphur on the stilbene, and it was found that when stilbene and sulphur are heated together at 250°, hydrogen sulphide is evolved and thionessal formed. Thionessal, which melts at 183—184°, is thus *tetraphenylthiophen*, $\begin{matrix}\mathrm{CPh{:}CPh}\\ |\\ \mathrm{CPh{:}CPh}\end{matrix}\!>\!\mathrm{S}$, and its formation is precisely analogous to that of thiophen itself on passing ethylene through boiling sulphur.

Tolallyl sulphide cannot be obtained by further heating stilbene or thionessal with sulphur, but is formed on heating benzyl sulphide or bisulphide, and by distilling phenylacetic acid with sulphur; it melts at 174°. It was shown by Raoult's method to have the formula $C_{14}H_{10}S$. Since tolallyl sulphide may be converted, by oxidation, into oxylepiden, which contains four phenyl groups, it must itself contain phenyl groups, and has, doubtless, the formula $\begin{matrix}\mathrm{CPh}\\ ||\\ \mathrm{CPh}\end{matrix}\!>\!\mathrm{S}$. A better name for it would be *tolane sulphide*. C. F. B.

Action of Nitrous Acid on Tetramethyldiamidobenzophenone. By W. Herzberg and M. Polonowsky (*Ber.*, **24**, 3197—3201).—By the action of nitrous acid on tetramethyldiamidobenzophenone, E. Bischoff (Abstr., 1888, 1197; 1889, 511) obtained a substance to which he assigned the constitution

$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_2(:NOH){\cdot}NMe_2}.$$

The authors find that when the reaction is carried out according to Bischoff's instructions, a yellow precipitate is formed, amounting to about 30 per cent. of the ketone taken; this crystallises from alcohol in yellow plates melting with evolution of gas at 182—183°. The compound has, however, the composition $C_{16}H_{17}N_3O_2$, and is, in reality, the *nitrosamine* of *trimethyldiamidobenzophenone*,

$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NMe{\cdot}NO}.$$

By the action of concentrated hydrochloric acid, it is converted into *trimethyldiamidobenzophenone*, $\mathrm{NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NHMe}$, which crystallises from alcohol in pale-yellow plates, melts at 203—204°, and yields an *acetyl* derivative, $C_{16}H_{17}N_2O_2Ac$, melting at 145°. The compound described by Wichelhaus (Abstr., 1886, 362) as trimethyldiamidobenzophenone is probably a mixture of the trimethyl and tetramethyl compounds. In Bischoff's experiments, he did not separate the precipitate, but added alkali, and thus obtained a mixture of the nitrosamine with unaltered ketone. If double the quantity of sodium nitrite be taken, the yield of nitrosamine can be raised to 60 per cent. of the ketone, a small quantity of a substance sparingly soluble in hot alcohol being then also obtained.

Nitrous acid acts in a different manner on tetramethyldiamidodiphenylmethane, converting it partially into paranitrodimethylaniline.

H. G. C.

Derivatives of Paraphenylbenzophenone. By G. Koller (*Monatsh.*, **12**, 501—511; compare Goldschmidt, *ibid.*, **2**, 437).—Paraphenylbenzophenoxime, $C_6H_4Ph{\cdot}CPh{:}NOH$, is obtained on treating paraphenylbenzophenone in alcoholic solution with an aqueous solution of hydroxylamine hydrochloride and potash. It crystallises in needles, melts at 193—194°, is insoluble in water, dissolves readily in alcohol and ether, and, when heated at 100° with a mixture of acetic acid and acetic anhydride saturated with hydrochloric acid, is converted into the isomeric acid-anilide, which melts at 224°, and is resolved into aniline and paraphenylbenzoic acid (m. p. 218—219°) when heated at 160° with fuming hydrochloric acid.

The *benzoyl derivative* of the oxime, $C_6H_4Ph{\cdot}CPh{:}NOBz$, crystallises from alcohol in slender, white needles, and melts at 193°. On treatment with sodium amalgam, the oxime is reduced to the amidobase, $C_6H_4Ph{\cdot}CHPh{\cdot}NH_2$, which crystallises from ether in slender, white needles, melts at 77°, and forms an *acetate* which crystallises in needles melting at 161°, a *hydrochloride* which melts at 252°, a *nitrate* which melts at 211°, and a *platinochloride* which crystallises in yellow needles containing 4 mols. H_2O, and melts at 191°.

The *phenylhydrazone*, $C_6H_4Ph{\cdot}CPh{:}N_2HPh$, is obtained by the action of phenylhydrazine on paraphenylbenzophenone, and crystallises from absolute alcohol in yellow needles which melt at 144°.

G. T. M.

Claus' Theory of the Benziloximes. By K. Auwers and V. Meyer (*Ber.*, **24**, 3267—3271).—Claus (this vol., p. 50) has recently put forward the view that the isomerism of the benziloximes is due to differences of molecular structure rather than to those of the relative positions in space of the atoms within the molecule (stereochemical isomerism), and in defending the latter hypothesis the authors state that Claus has not taken into account the following facts:—Benzophenone and its symmetrical di-substitution derivatives yield only one oxime, whereas its mono-substitution derivative yields two, for which reason such formulæ as those proposed by Claus for the benziloximes are inadmissible for the benzophenonoximes, and it is specially to be noted that the isomerism of the oximes of both series have been proved by numerous experiments to be strictly analogous.

Claus represents benzile-α-monoxime as a true oximido-derivative, $CPh{\cdot}C(:NOH){\cdot}COPh$, and benzile-$\gamma$-monoxime as a nitroso-alcohol, $CPh{\cdot}C(NO){:}CPh{\cdot}OH$, and such a difference of structure would necessitate a corresponding difference in chemical behaviour, but the single fact which Claus adduces is that the α-derivative is converted by an excess of hydroxylamine with greater ease into a dioxime than is the γ-derivative; this being a difference of degree and not of kind. In reality, the α-derivative reacts with both hydroxylamine and its hydrochloride, whereas the γ-derivative only reacts with the free base; towards all other reagents the two compounds show complete similarity in their behaviour; apart from

this, however, the formula ascribed by Claus to the γ-monoxime is incompatible with the facts to be mentioned. It is well known that isonitroso-compounds (oximes) are more stable than true nitroso-derivatives, and it is difficult to understand why a nitroso-derivative is formed by a reaction which should yield an oxime as the direct product, and also that the same oxime is converted into a nitroso-derivative on heating its alcoholic solution at 100°; it is necessary to admit both of these, however, on Claus' hypothesis. Claus' formula for the γ-benzilemonoxime is entirely negatived by the observation that the benzyl-derivative of this oxime is formed by the interaction of α-benzylhydroxylamine and benzile (Abstr., 1889, 1193), thus: $\begin{matrix}\mathrm{Ph{\cdot}CO}\\ \mathrm{Ph{\cdot}CO}\end{matrix} + \mathrm{NH_2{\cdot}O{\cdot}CH_2Ph} = \begin{matrix}\mathrm{Ph{\cdot}C{:}NO{\cdot}CH_2Ph}\\ \mathrm{Ph{\cdot}CO}\end{matrix}$; whereas to admit that a compound of the formula $\begin{matrix}\mathrm{PhC{\cdot}NO}\\ \mathrm{PhC{\cdot}O{\cdot}CH_2Ph}\end{matrix}$ is produced would at once render it impossible to rely on the constitution of a compound which had been deduced from synthetical considerations. If, therefore, one of the benzilemonoximes is a nitroso-alcohol, it can only be the unstable α-modification, the benzyl derivative of which has not, up to the present, been prepared from benzile and α-benzylhydroxylamine, but then from this nitroso-alcohol (the α-monoxime), the α-dioxime, which Claus regards as a true dioxime, would be formed on treating it with hydroxylamine; whilst the true monoxime (the γ-monoxime) would be converted into the nitrosohydroxylamide $\begin{matrix}\mathrm{Ph{\cdot}C{\cdot}NO}\\ \mathrm{Ph{\cdot}C{\cdot}NH{\cdot}OH'}\end{matrix}$, which, according to Claus, represents the γ-dioxime. The authors dismiss the three benzildioximes with only a few remarks, and conclude with the statement that, as their investigations on all these compounds have shown that they have the same structure, they have no other alternative, in accordance with the present views, than to regard the isomerism as stereochemical.

A. R. L.

Dyes of the Triphenylmethane Group. By E. Noelting (*Ber.*, 24, 3126—3136; 3136—3139; 3139—3143; compare Abstr., 1891, 727).—*Tetramethyltriamidodiphenyltolylmethane*,

$$\mathrm{\overset{3}{N}H_2{\cdot}C_6H_3\overset{6}{M}e{\cdot}\overset{1}{C}H(C_6H_4{\cdot}\overset{4}{N}Me_2)_2},$$

is prepared by mixing finely powdered tetramethyldiamidobenzhydrol (27 grams) with cooled concentrated sulphuric acid (270 grams), adding paratoluidine (11 grams), raising the temperature to 40—50° to complete dissolution, and finally heating on the water-bath at 50—60° for 6 to 8 hours. The product is poured into water (3 litres), cautiously neutralised with soda, and any unaltered paratoluidine driven over with steam; the base is then dissolved in hydrochloric acid, reprecipitated with ammonia, extracted with ether, and light petroleum added to the dried ethereal solution to incipient turbidity, it being then placed over sulphuric acid in a vacuum, when the leucobase slowly separates in the form of white needles, the yield being 90—95 per cent. of the theoretical. It melts at 160°, is sparingly

soluble in light petroleum, more readily in ether and alcohol, and insoluble in water. On oxidation with lead peroxide, it yields a bluish-green, soluble dye, homologous with metamidobenzaldehyde-green. The *dibenzyl derivative*, $C_{24}H_{27}N_3(C_7H_7)_2$, is obtained by boiling the leuco-base (1 mol.) with benzyl chloride (2·5 mols.), sodium acetate (1 mol.), and water (6—7 parts), in a reflux apparatus for 8—10 hours, the excess of benzyl chloride being then driven over with steam; it is dissolved in hydrochloric acid (1 : 5), concentrated hydrochloric acid added, whereby the hydrochloride melting at 186° separates in white needles, or, for the preparation of the free base, it is preferably converted into the zincochloride, from which the base is obtained on treatment with ammonia. The base, when crystallised from a mixture of ether and light petroleum, melts at 120°, is not acted on by acetic anhydride, yields a greenish-blue dye on oxidation, and is converted into sulphonic acids by the action of fuming sulphuric acid; these give bluish-green dyes on oxidation which colour wool and silk in an acid-bath. When the first-mentioned leuco-base is ethylated, and subsequently oxidised, a bluish-green dye is likewise obtained. The presence of the methyl group in the ortho-position relatively to the fundamental carbon atom appears to have the effect of rendering the derived dye much bluer than those from the lower homologue. The *phenol*, $\overset{3}{OH}\cdot C_6H_3\overset{6}{Me}\cdot CH(C_6H_4\cdot\overset{1}{N}Me_2)_2$, is obtained by dissolving the leuco-base (36 grams) in a mixture of concentrated sulphuric acid (70 grams) and water (3 litres), diazotising the cooled solution with sodium nitrite (7 grams), heating on the water-bath, precipitating with ammonia, and finally extracting with ether; it separates from a mixture of ether and light petroleum in white needles, melts at 156°, and is sparingly soluble in light petroleum and aqueous alkalis, easily in ether, alcohol, and acids, but insoluble in water; on oxidation, it yields a dye of a less bluish shade than those obtained from the amido-derivative.

Tetramethyltriamidodiphenyltolylmethane,

$$\overset{2}{N}H_2\cdot C_6H_3\overset{5}{Me}\cdot\overset{1}{C}H(C_6H_4\cdot\overset{4}{N}Me_2)_2,$$

is produced by heating a mixture of tetramethyldiamidobenzhydrol, paratoluidine, hydrochloric acid of 22° Baumé (27 grams of each), and water (100 c.c.) on the water-bath for 12—15 hours. The pure leuco-base crystallises from alcohol in needles, and melts at 180°, the yield being 75—80 per cent. of the theoretical. It gives a faint, bluish-violet dye on oxidation; the *dibenzyl derivative* is less readily oxidised than the above-described isomeride, whilst, on oxidising the *diacetyl derivative*, a green dye is obtained, which, on treatment with hydrochloric acid or alcoholic soda, is converted into a bluish-green dye with the elimination of the acetyl groups. The corresponding *phenol* crystallises from a mixture of light petroleum and ether in white needles, melts at 129—130°, and is more soluble in light petroleum than its isomeride; its constitution is proved by the fact that it is obtained by condensing homosalicylaldehyde with dimethylaniline in the presence of zinc chloride.

The condensation of asymmetrical-metaxylidine, mesidine, ψ-cum-

idine, isoduridine, and prehnidine (consecutive tetramethylaniline) with tetramethyldiamidobenzhydrol has also been effected by the author. In the presence of sulphuric acid, asymmetrical metaxylidine yields a leuco-base melting at 158°, and giving a green dye of a less bluish shade than that obtained from paratolnidine; mesidine, a leuco-base melting at 142°, giving a green dye of a more bluish shade; whilst ψ-cumidine and isoduridine yield leuco-bases melting at 132° and 157° respectively, the former giving a green dye of a very bluish shade, and the latter one of a less bluish shade. The reaction proceeds with difficulty with prehnidine, and the leuco-base withstands oxidation to a marked extent. In the presence of hydrochloric acid, asymmetrical metaxylidine yields a leuco-base melting at 145°, and ψ-cumidine one melting at 163—164°; both behave towards oxidising agents like the base from prehnidine, whilst mesidine and isoduridine yield the same products as in the presence of sulphuric acid.

Tetrethyltriamidodiphenyltolylmethane,

$$NH_2{\cdot}C_6H_3Me{\cdot}CH(C_6H_4{\cdot}NEt_2)_2,$$

prepared from tetrethyldiamidobenzhydrol and paratoluidine in the presence of concentrated sulphuric acid, melts at 103°, and yields a dye of a less bluish shade than that of the corresponding tetramethyl derivative.

The base obtained from tetramethyldiamidobenzhydrol and dibenzylparatoluidine in the presence of sulphuric acid is entirely different from the above-described dibenzyltetramethyltriamidodiphenyltolylmethane; it yields a pure green dye on oxidation, and condensation has perhaps taken place in the benzyl residue; that such is possible is proved by the fact that benzylamine condenses with the hydrol under the same conditions, and the product yields a green dye on oxidation.

Paranitrodimethyldiamidodiphenyltolylmethane,

$$\overset{3}{N}H_2{\cdot}C_6H_3\overset{6}{M}e{\cdot}\overset{1}{C}H(C_6H_4{\cdot}\overset{4}{N}Me_2){\cdot}C_6H_4{\cdot}\overset{4}{N}O_2,$$

is prepared by dissolving paranitrodimethylamidobenzhydrol (27 grams) in concentrated sulphuric acid (300 grams), adding paratoluidine (20 grams), and heating the mixture on the water-bath at 60—70° for 12 hours. The base separates from a mixture of alcohol and benzene in yellow needles, and melts at 202°; on oxidation with lead peroxide or chloranil, a brown dye is obtained which only imparts a faint colour to cotton mordanted with tannin; the presence of an amido-group in the meta-position relatively to the fundamental carbon atom appears to hinder the ready oxidation of the compound. The acetyl derivative crystallises in white needles, and, on oxidation with chloranil, yields a dye, which colours mordanted cotton orange-red; the shade remains unaltered when the acetyl groups are eliminated by heating the dye with acids.

Dimethyltriamidodiphenyltolylmethane,

$$\overset{3}{N}H_2{\cdot}C_6H_3\overset{6}{M}e{\cdot}\overset{1}{C}H(C_6H_4{\cdot}\overset{4}{N}Me_2){\cdot}C_6H_4{\cdot}\overset{4}{N}H_2,$$

is obtained by reducing the last-described nitroleuco-base with tin and hydrochloric acid; it crystallises from a mixture of ether and light petroleum in white needles, melts at 154°, and, on oxidation with lead peroxide, yields a bluish-green dye; whereas the acetyl derivative, on oxidation with chloranil, yields a dye colouring cotton mordanted with tannin a beautiful red. When the base is dissolved in methyl alcohol and heated in a reflux apparatus with methyl iodide and soda, *hexamethyltriamidodiphenyltolymethane* is formed; it crystallises from a mixture of ether and light petroleum in white plates, melts at about 100°, and yields a bluish-green dye on oxidation.

Tetramethyltriamidotriphenylmethane, prepared by the condensation of paranitrobenzaldehyde with dimethylaniline, and also from tetramethyldiamidobenzhydrol and aniline (D.R.-P. 27032), melts at 151—152°, and not at 65° as stated by Nathansohn and Müller (Abstr., 1889, 1190); it has, furthermore, the constitution

$$\overset{4}{\mathrm{NH_2}}\cdot\mathrm{C_6H_4}\cdot\overset{1}{\mathrm{CH}}(\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2})_2;$$

the compound of the constitution given by Nathansohn and Müller is described by O. Fischer and Schmidt (Abstr., 1884, 1315), and melts at 134—135°; the methiodide melts at 193° with decomposition.

Tetramethyldiamidodiphenylquinolylmethane,

$$\mathrm{C_9NH_6}\cdot\overset{3,1}{\mathrm{CH}}(\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2})_2,$$

is obtained by heating a mixture of tetramethyltriamidotriphenylmethane (4 grams), glycerol (3·8 grams), sulphuric acid (6 grams), and nitrobenzene (0·9 gram) at 140—150° for 10—12 hours. It crystallises from alcohol in white needles which become greenish in the air, melts at 165°, is soluble in ether and benzene, and insoluble in light petroleum and water, and yields a green dye on oxidation; the *hydrochloride*, $\mathrm{C_{26}H_{27}N_3,3HCl}$, is readily soluble, and the *platinochloride* sparingly soluble, in water.

Tetramethyltriamidodiphenylmethoxytolylmethane,

$$\overset{4}{\mathrm{N}}\mathrm{H_2}\cdot\mathrm{C_6H_2}\overset{2}{\mathrm{Me}}(\overset{5}{\mathrm{O}}\mathrm{Me})\cdot\overset{1}{\mathrm{CH}}(\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2})_2,$$

is prepared by heating a mixture of tetramethyldiamidobenzhydrol (10 grams), amidomethylmethoxybenzene, $\mathrm{NH_2\cdot C_6H_3Me\cdot OMe}$ [2 : 4 : 1] (5·3 grams), and 36 per cent. hydrochloric acid (10·3 grams) on the water-bath for 4 hours; it crystallises in white needles, melts at 158—159°, is somewhat sparingly soluble in alcohol and ether, and very readily in benzene, and yields a beautiful blue dye on oxidation.

Tetramethyldiamidodiphenylmethoxymethylquinolylmethane,

$$\mathrm{C_9N}\overset{4}{\mathrm{H_3}}\overset{2}{\mathrm{Me}}(\mathrm{OMe})\cdot\overset{3,1}{\mathrm{CH}}(\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2})_2,$$

is prepared from the last described base, it being, however, found expedient to employ picric acid instead of nitrobenzene in its preparation; the compound crystallises from a mixture of light petroleum

and benzene in white needles, melts at 183°, and yields a green dye on oxidation. A. R. L.

Benzeneazo-α-naphthylglycocine. By A. Donner (*Ber.*, **24**, 2902—2904).—Azo-dyes have previously only been prepared from substituted amines in which the amido-hydrogen atom is replaced by alkyl groups. The author has now obtained azo-dyes from amines in which the amido-hydrogen atom is replaced by a group containing carboxyl group.

Benzeneazo-α-naphthylglycocine is prepared by adding a solution of α-napthylglycocine, dissolved in dilute hydrochloric acid, to a solution of diazobenzene chloride at a temperature not exceeding 0°. After remaining 12 hours, the *hydrochloride* of the new compound separates as a dark-brown, crystalline precipitate; it is collected, washed with dilute hydrochloric acid, and dried. It crystallises from alcohol in needles, melts at 170° with evolution of gas, is sparingly soluble in water, more so in concentrated hydrochloric acid, and easily in alcohol. The solutions are intense reddish-blue and turn yellowish-red on the addition of alkalis. In concentrated sulphuric acid, it dissolves with a deep-blue coloration, which changes to violet on the addition of water. The hydrochloric acid solution dyes silk a violet colour. By continued washing with water, the hydrochloride undergoes partial decomposition into the free base.

Benzeneazo-α-naphthylglycocine behaves as an amido-acid, and forms salts both with acids and bases. The *potassium salt* is obtained by adding a slight excess of potassium hydroxide to the hydrochloride. It crystallises in bronze-red tablets which rapidly discolour in the air, and must be dried in a vacuous desiccator over calcium chloride and potassium hydroxide; it dissolves easily in alcohol and warm water, more sparingly in the cold. The aqueous solution gives, with silver nitrate, a red, and with copper sulphate, a brown precipitate. The *ammonium salt* is prepared in a similar way to the potassium salt and crystallises in well formed, yellowish-red needles. Silk is dyed golden-yellow by solutions of the alkali salts.

The *free base* is best prepared by adding the theoretical quantity of potassium hydroxide to a solution of the hydrochloride, evaporating to dryness, and extracting with alcohol. It crystallises in small, lustrous, green needles, melts at 133° with evolution of gas, and is sparingly soluble in water, more easily in alcohol and ether. The solution is brown. The free base can also be prepared by decomposing the potassium salt with carbonic acid, but at the same time a compound is formed which crystallises in reddish-brown needles and which the author believes to have the constitution

$$N_2Ph\cdot C_{10}H_6\cdot NH\cdot CH_2\cdot COONH_2(CH_2\cdot COOK)\cdot C_{10}H_6\cdot N_2Ph.$$

E. C. R.

Hydronaphthoic Acids. By A. v. Baeyer, R. Schoder, and E. R. Besemfelder (*Annalen*, **266**, 169—202).—This paper has been published somewhat sooner than was intended because of the appearance of an article by v. Sowinski (Abstr., 1891, 1380) on the same subject; it will be seen by comparing the two papers that there are numerous points of disagreement between them, for which reason the

authors think that the publication of their results is by no means a superfluous proceeding.

Labile Δ^2-dihydro-α-naphthoic acid [COOH = 1] is obtained by dissolving α-naphthoic acid (5 grams) and the theoretical quantity of sodium carbonate in water (50 c.c.) and then adding 4 per cent. sodium amalgam (60 grams) to the well-cooled solution, through which a stream of carbonic anhydride is at the same time passed; when the solution is found to be free from naphthoic acid, it is neutralised with dilute sulphuric acid, filtered, mixed with excess of sulphuric acid, and the precipitated acid purified by means of its barium salt, which is very readily soluble in water (the impurities remaining undissolved). It crystallises from light petroleum in slender, colourless, monoclinic needles, melts at 91°, and is readily soluble in ether, ethyl acetate, alcohol, and carbon bisulphide, but more sparingly in benzene, light petroleum, and cold water (1 in 552 parts); it seems to be decomposed by boiling water, and, unlike the $\Delta^{2:5}$-dehydroterephthalic acid, with which it has many properties in common, it immediately decolorises an alkaline solution of potassium permanganate, being converted into phthalic acid, resinous products, and an acid which has the odour of acetic acid. The silver salt separates from water in reddish needles. The dibromide, $C_{10}H_9Br_2{\cdot}COOH$, prepared by treating the acid with bromine in well-cooled carbon bisulphide solution, separates from a mixture of ether and light petroleum in the form of a crystalline powder, melts at 132°, and is readily soluble in ether and carbon bisulphide, but more sparingly in benzene and light petroleum; it is stable towards potassium permanganate, the violet colour disappearing only on prolonged keeping. It is readily reduced by zinc-dust and glacial acetic acid, being reconverted into the original dihydro-acid, and when warmed with alcoholic potash, it yields naphthoic acid. Stable Δ^1-dihydro-α-naphthoic acid is formed when the labile acid is boiled for a few hours with soda; it separates from ethyl acetate in well-defined, monoclinic crystals, $a : b : c = 1{\cdot}5399 : 1 : 1{\cdot}5657$, $\beta = 59°\ 12'$, melts at 125°, and is moderately easily soluble in alcohol, but only very sparingly (1 in 3512 parts) in cold water. The silver salt crystallises from hot water in colourless needles, which soon turn reddish on exposure to the air. The acid is immediately oxidised by potassium permanganate, yielding orthocarboxyhydrocinnamic acid (m. p. 165°) and small quantities of phthalic acid; the formation of the first-named compound proves that the dihydro-acid has the constitution assigned to it above. The dibromide separates from a mixture of ether and light petroleum in yellowish crystals, melts at 152°, and is reconverted into the original dihydro-acid on reduction with zinc-dust and glacial acetic acid; it is very stable towards potassium permanganate, but is decomposed by boiling methyl alcoholic potash yielding α-naphthoic acid and the dihydro-acid.

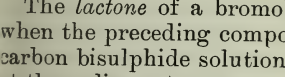
Tetrahydro-α-naphthoic acid is formed when α-naphthoic acid or either of its dihydro-derivatives is treated with sodium amalgam in warm alkaline solution; when reduction is at an end, the neutralised solution is filtered and then treated with sodium carbonate and potassium permanganate until the solution retains its violet colour

for a short time. The acid is then precipitated with sulphurous and sulphuric acids and repeatedly recrystallised from ethyl acetate, from which it separates in well-defined, triclinic crystals, melting at 85°; it is soluble in 1052 parts of cold water, and is moderately stable towards potassium permanganate, the violet colour disappearing only after keeping for a few minutes. The silver salt crystallises from hot water, in which it is moderately easily soluble, in colourless needles, which soon assume a reddish hue. When the chloride of the acid is treated with bromine in the cold and the product then warmed with concentrated formic acid, a yellow, crystalline compound, seemingly a monobromo-substitution product of the tetrahydro-acid, is obtained. The *amide* crystallises from alcohol in colourless needles, and melts at 116°.

Two dihydro-acids are formed when β-naphthoic acid is reduced with sodium amalgam as described in the case of the corresponding α-compound (except that potassium carbonate is used instead of the sodium salt); on acidifying, the two acids are precipitated in an oily condition, but this oil quickly solidifies, and, after recrystallisation from hot water, a seemingly homogeneous substance melting at 103—104° is obtained; it is possible, however, by fractional precipitation to resolve this product into the two acids described immediately below.

Labile Δ^3-dihydro-β-naphthoic acid crystallises from dilute alcohol in microscopic, seemingly rhombic prisms, melts at 104—105°, and is soluble in 1734 parts of water at 14°; it is immediately oxidised by potassium permanganate in sodium carbonate solution, yielding phthalic acid and oxalic acid, but on oxidation with potassium ferricyanide it is reconverted into β-naphthoic acid. The silver salt is decomposed by boiling water.

The *lactone* of a bromohydroxytetrahydronaphthoic acid is formed when the preceding compound is treated with bromine in well-cooled carbon bisulphide solution in the dark, the solution then evaporated at the ordinary temperature (whereon hydrogen bromide is evolved), the yellowish-red residue dissolved in ether, and the solution shaken with sulphurous acid and sodium carbonate successively. It separates from ether in monoclinic crystals, melts at 124° with decomposition, and is insoluble in cold sodium carbonate; when treated with zinc-dust and glacial acetic acid, it is reconverted into the labile dihydro-acid, and alcoholic potash transforms it into β-naphthoic acid. This lactone has, doubtless, the constitution represented by the formula



, and its formation from the labile acid shows that the latter is the Δ^3-dihydro-derivative; the dibromide, from which the lactone is produced, could not be obtained in crystals.

Stable dihydro-β-naphthoic acid is formed when the labile acid is boiled with soda, but the conversion is never complete, and, in presence of air, naphthoic acid is also formed; it is, therefore, more conveniently prepared by boiling a solution of the potassium salt of β-naphthoic acid with 3 per cent. sodium amalgam, until the whole of the naphthoic acid has been reduced. The stable acid is then separated

from its isomeride and from tetrahydronaphthoic acid by fractionally precipitating its solution in decinormal ammonia with hydrochloric acid of the same concentration. It crystallises from boiling benzene in small, colourless, nacreous plates, melts at 161°, and is very sparingly soluble (1 in 19318 parts) in water at 14°; it dissolves freely in alcohol, ether, and glacial acetic acid, but is more sparingly soluble in benzene and light petroleum, and very sparingly in carbon bisulphide. On oxidation with an alkaline solution of potassium ferricyanide, it yields β-naphthoic acid, and its cold solution in sodium carbonate immediately decolorises potassium permanganate, the crystalline products being phthalic acid and oxalic acid. The silver salt is amorphous and is decomposed by boiling water. The dibromide, $C_{11}H_{10}Br_2O_2$, is formed, without evolution of hydrogen bromide, when the acid is treated with bromine in well-cooled chloroform solution in the dark; it separates from a mixture of light petroleum and ether in monoclinic crystals, melts at 208°, dissolves freely in sodium carbonate, and is very stable towards potassium permanganate. It is readily soluble in alcohol, chloroform, glacial acetic acid, and hot water, but only moderately in ether and light petroleum, and sparingly in cold water; when warmed with alcoholic potash, it is converted into β-naphthoic acid, and on treatment with zinc-dust and glacial acetic acid, it seems to be transformed into the dihydro-acid from which it is derived. This stable dihydro-acid is either the Δ^2- or the Δ^1-derivative, probably the former. Tetrahydro-β-naphthoic acid is best obtained by heating an alkaline solution of β-naphthoic acid with sodium amalgam until the permanganate test shows the absence of oxidisable substances; the precipitated acid is dissolved in sodium carbonate, and potassium permanganate added until a violet coloration is produced, by which means the product is obtained free from all traces of the dihydro-acids. It crystallises from dilute alcohol and boiling water in transparent needles, melts at 96°, and is soluble in 1661 parts of water at 14°; it does not reduce a warm ammoniacal solution of silver nitrate, and its cold solution in sodium carbonate does not immediately decolorise potassium permanganate. It is only slowly oxidised by an alkaline solution of potassium ferricyanide, and it does not combine with bromine in cold chloroform solution in the dark; on oxidation with potassium permanganate at the ordinary temperature, it yields oxalic acid and phthalic acid. The silver salt is more readily soluble than the salts of the dihydro-acids.

The electrical conductivity of the acids described in this paper was measured by Bethmann and Bader with the following results:—

α-Naphthoic acid	K = 0·0197	β-Naphthoic acid	K = 0·00523
Δ^1-Dihydro-α-acid	K = 0·0080	Δ^2-Dihydro-β-acid ...	K = 0·00290
Δ^2-Dihydro-α-acid	K = 0·0114	Δ^3-Dihydro-β-acid ...	K = 0·00515
Tetrahydro-α-acid	K = 0·00445	Tetrahydro-β-acid ...	K = 0·00250

F. S. K.

α-Naphthol-α-sulphonic Acid. By O. N. Witt and H. Kaufmann (*Ber.*, **24**, 3157—3163).—α-Naphthol-α-sulphonic acid is prepared on a technical scale by boiling diazotised naphthionic acid with dilute sulphuric acid (Neville and Winther, *Ber.*, **13**, 1949), or by

fusing naphthionic acid with sodium hydroxide under pressure (D R.-P. 46307); the products from the two methods are dissimilar in appearance, as are also to some extent the azo-dyes obtained from them, but the latter, after repeated crystallisation, are found to be identical. On reducing these dyes with an acid solution of stannous chloride (Witt, Abstr., 1889, 270), a sparingly soluble amidonaphtholsulphonic acid separates, after a time, in the form of iridescent, greyish needles and plates; this can be purified by repeatedly dissolving in disodium sulphite solution, reprecipitating by hydrochloric acid and finally washing with water, alcohol, and ether; it contains 1 mol. H_2O. It is probable that the impurity in the naphtholsulphonic acid prepared by the fusion method is due to the presence of an isomeride, which may perhaps be produced by intramolecular change during the fusion, but the acid prepared by Neville and Winther's method also contains an impurity, the nature of which has not as yet been determined.

β-Nitroso-α-naphthol-α-sulphonic acid is obtained when sodium α-naphthol-α-sulphonate (24·6 grams) is dissolved in water (300 c.c.), 39 per cent. hydrochloric acid (19 c c.) added, and sodium nitrite (6·9 grams) in concentrated solution slowly dropped into the cooled mixture; the precipitated compound is collected and crystallised from a mixture of water (500 c.c.) and hydrochloric acid (50 c c.), when it separates in brownish-yellow, lustrous crystals, the yield being 20 grams. It contains $3\frac{1}{2}$ mols. H_2O, and is rendered anhydrous at 115°, after which it is very hygroscopic; it is easily soluble in water and alcohol; concentrated sulphuric acid dissolves it with an orange-red colour, which, on dilution, becomes yellow, whilst nitric acid, on heating, converts it into dinitronaphthol. The acid dissolves in ammonia and in sodium hydroxide solution with a reddish-brown colour, forming the *normal salts*, and from these solutions, on addition of barium chloride and alcohol, a gelatinous *barium salt* is precipitated. The *salt*, $OH{\cdot}C_{10}H_5(NO){\cdot}SO_3Na$, separates on adding an excess of sodium acetate to the hot aqueous solution of the acid in the form of orange-yellow needles and prisms; the *barium salt*, $(C_{10}H_6NSO_5)_2Ba + 3H_2O$, is precipitated in small, vermilion crystals on adding barium chloride to a solution of the preceding sodium salt. The acid gives a red colour with cobalt salts and a green colour with iron salts; when heated with aniline, naphthaquinonedianilide (Zincke, Abstr., 1882, 967) is formed. It reacts with orthodiamines with the production of scarlet dyes, probably belonging to the eurhodine group; the base obtained with 1 : 2-diamidotoluene forms golden-yellow needles, and melts at 257°. On careful reduction with acid stannous chloride solution, or when heated with sodium hydrogen sulphite solution, it yields the same amidonaphtholsulphonic acid as the azo-dyes derived from α-naphthol-α-sulphonic acid (see above), and must therefore have the constitution [OH : NO : SO_3H = 1 : 2 : 4].

Sodium β-naphthaquinone-α-sulphonate, $C_{10}H_5O_2{\cdot}SO_3Na$, is prepared by gently heating the last-mentioned amidonaphtholsulphonic acid (5 grams) with nitric acid, sp. gr. 1·4 (10 c.c.), and adding a saturated solution of sodium chloride (40 c.c.); it separates in yellow needles, and is crystallised from dilute alcohol; it is readily soluble in water

and almost insoluble in alcohol; sulphurous acid converts it into the corresponding quinol-derivative. The quinone reacts with 1 : 2-diamidotoluene, forming an azine which crystallises in red needles, thus proving its constitution. A. R. L.

Sulphonic Acids of β-Naphthaquinone. By O. N. Witt (*Ber.*, **24**, 3154—3157).—The amidonaphtholsulphonic acids are very readily oxidised; thus, in alkaline solution they are converted by the oxygen of the air into greenish-brown compounds, which may be derivatives of β-naphthaquinhydrone; in acid solution, when ferric chloride or potassium dichromate is used as the oxidising agent, β-naphthaquinonesulphonic acids appear to be formed, which cannot, however, be isolated on account of their great affinity for these metals.

Ammonium β-naphthaquinonesulphonate, $C_{10}H_5O_2{\cdot}SO_3NH_4$, is obtained by adding amido-β-naphthol-β-sulphonic acid (10 grams) in small portions at a time to nitric acid, sp. gr. 1·2 (10 c.c.); the semi-solid product is spread upon a porous tile, and finally crystallised from a very small quantity of water, the solution being cooled by ice; in this way, a product, representing 60—75 per cent. of the starting material, is obtained in the form of golden-yellow needles; it is dried at 100—110°. The compound is very soluble in water and somewhat less so in alcohol; on treating it with sodium hydroxide, the sodium salt is formed, but an excess of the alkali decomposes it; it reacts with orthodiamines with the formation of azinesulphonic acids. The corresponding quinol-derivative is formed when the salt is reduced with aqueous sulphurous acid, but it is more conveniently prepared as follows:—The amidonaphtholsulphonic acid is mixed with water and the calculated quantity of bromine added; to the solution of the quinone, an excess of sulphurous acid is now added, and the ammonium quinolsulphonate isolated by evaporating the solution; it forms white plates, and is very easily soluble in water; alkalis colour its aqueous solution deep-yellow, and ammonia in the presence of air deep-brown; silver salts are immediately reduced, and it is not oxidised to the quinone by nitric acid of sp. gr. below 1·2. When oxidised in the presence of paradiamines, violet-red dyes, belonging to the group of indophenols, are produced, and it reacts with diazo-compounds with the formation of azo-dyes which yield brownish-red to indigo-blue lakes with metallic mordants. It thus furnishes an exception to the observations that orthodihydroxy-compounds are not capable of forming azo-dyes. The other amidonaphtholsulphonic acids yield similar compounds on oxidation. A. R. L.

Phenanthridine. By H. Pictet and H. J. Ankersmit (*Annalen*, **266**, 138—153; compare Abstr., 1891, 837).—Attempts to synthesise phenanthridine by treating orthohydroxybenzylideneaniline,

$$OH{\cdot}C_6H_4{\cdot}CH{:}NPh,$$

and benzylideneorthamidophenol, $OH{\cdot}C_6H_4{\cdot}N{:}CHPh$, with dehydrating agents were unsuccessful; both compounds seem to yield small quantities of acridine on distillation over zinc-dust.

Benzylideneorthamidophenol, $C_{13}H_{11}NO$, prepared by the condensa-

tion of benzaldehyde and orthamidophenol, crystallises from alcohol in grey, hexagonal plates, melts at 89°, and is readily soluble in ether and benzene, but insoluble in water.

Hydroxyphenanthridine, $\begin{matrix}C_6H_4\cdot C(OH)\\ \vert \quad\quad \Vert \\ C_6H_4\cdot N\end{matrix}$, prepared as previously described (*loc. cit.*), crystallises from alcohol in colourless needles, melts above 290°, and is insoluble in cold water, ether, benzene, and alkalis.

Phenanthridine methyl hydroxide, $C_{13}H_9N,MeOH$, prepared by decomposing the methiodide (Abstr., 1890, 390) with alcoholic soda, crystallises in colourless needles, melts at 109°, and dissolves freely in alcohol, ether, and mineral acids, yielding fluorescent solutions.

Dihydrophenanthridine, $\begin{matrix}C_6H_4\cdot CH_2\\ \vert \quad\quad \vert \\ C_6H_4\cdot NH\end{matrix}$, is obtained when phenanthridine hydrochloride is treated with tin and hydrochloric acid; it crystallises from dilute alcohol in colourless needles, melts at 90°, and is almost insoluble in water, but very readily soluble in alcohol and ether, yielding fluorescent solutions. It is readily oxidised, even on exposure to the air, being reconverted into phenanthridine. The *mercurochloride* crystallises from hot water in needles and melts at 204°. The *platinochloride* decomposes at about 220°, but without melting. The *picrate* and the *dichromate* crystallise from hot water in slender, yellow needles. The *nitroso*-derivative is an oil. The *acetyl* derivative, $C_{15}H_{13}NO$, crystallises in colourless prisms melting at 108°.

F. S. K.

Methylphenanthridine and Chrysidines. By A. Pictet and S. Erlich (*Annalen*, **266**, 153—168; compare Abstr., 1891, 217).—*Paramethylphenanthridine*, $\begin{matrix}C_6H_4\text{—}\text{—}CH\\ \vert \quad\quad\quad \Vert \\ C_6H_3Me\cdot N\end{matrix}$ [N : Me : : = 2 : 5], is formed, together with benzene, toluene, &c., when the vapour of benzylideneparatoluidine is passed over red-hot pumice; it is isolated by means of its mercurochloride. It crystallises from dilute alcohol in long, colourless needles, melts at 131°, and is readily soluble in alcohol, ether, benzene, chloroform, and light petroleum, but only very sparingly in water; its aqueous and alcoholic solutions show a slight, blue fluorescence. The *hydrochloride* is readily soluble in water, from which it crystallises in yellow needles; the *sulphate* and the *nitrate* are also readily soluble. The *platinochloride*, $(C_{14}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles, loses its water at 110°, does not melt below 280°, and is decomposed by hot water. The *mercurochloride* forms yellow needles, melts at 215°, and is sparingly soluble in cold water, the solution showing a green fluorescence. The *aurochloride* crystallises in yellow needles melting at 210° with previous decomposition. The *picrate* and the *dichromate* crystallise in needles. The *methiodide*, $C_{14}H_{11}N,MeI$, crystallises from warm alcohol in brown needles melting at 180° with decomposition. The *methyl hydroxide*, $C_{14}H_{11}N,MeOH$, crystallises from dilute alcohol in colourless needles, melts at 136°, and is almost insoluble in water. The *methochloride* crystallises in yellow needles, and is only sparingly soluble in cold water.

Orthomethylphenanthridine, $C_{14}H_{11}N$ [N : Me = 2 : 3], is obtained when the vapour of benzylideneorthotoluidine is passed over red-hot pumice, but the principal product is α-phenylindole (compare Abstr., 1886, 711); it melts at about 70°, is not easily obtained in crystals, and is very readily soluble in alcohol, ether, chloroform, benzene, and light petroleum. The *hydrochloride* crystallises from water in slender, yellow needles, and dissolves freely in cold water, the dilute solutions showing a blue fluorescence. The *platinochloride*, $(C_{14}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles and does not melt below 275°. The *mercurochloride* (m. p. 196°), *aurochloride* (m. p. 196—200°), and the *picrate* (m. p. 220° with decomposition) crystallise in yellow needles: the *dichromate* crystallises from hot water in small, orange-red needles. The *methiodide*, $C_{14}H_{11}N,MeI$, separates from alcohol in brownish-yellow needles, melts at 187° with decomposition, and is readily soluble in alcohol and water, but only very sparingly in ether.

α-Chrysidine (Abstr., 1891, 217) crystallises from alcohol in needles, melts at 108°, and is readily soluble in ether, chloroform, and light petroleum, but insoluble in water. The *hydrochloride* crystallises from hot dilute hydrochloric acid in yellow needles, and melts at about 210°. The *nitrate* forms yellow prisms melting at 155°. The *platinochloride*, $(C_{17}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in long, yellow needles, and decomposes at 255°. The *mercurochloride* (m. p. 240—245°), the *aurochloride* (m. p. 228°), and the *picrate* (m. p. 240°) crystallise in yellow needles; the *dichromate* and the zinc double salt (m. p. about 250°) are also crystalline. The *methiodide*, $C_{17}H_{11}N,MeI$, crystallises from alcohol in pale yellow needles, melts at 108°, and is insoluble in ether. The *methyl hydroxide*, $C_{17}H_{11}N,MeOH$, forms colourless needles, and melts at 110°. The *methochloride* crystallises from dilute hydrochloric acid in long, slender needles; its *mercurochloride* melts at 215°, and its *platinochloride*, $(C_{17}H_{11}N)_2,Me_2PtCl_6$, crystallises in yellow needles.

β-Chrysidine (*loc. cit.*) crystallises from alcohol in lustrous, colourless needles, melts at 131°, and resembles the corresponding α-derivative in its properties. The *hydrochloride* crystallises in small, yellow prisms, and melts at about 220°. The *nitrate* is sparingly soluble, and forms yellow needles melting at 187°. The *platinochloride*, $(C_{17}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles, and melts at 245° with decomposition. The *dichromate*, $(C_{17}H_{11}N_2)_2,H_2Cr_2O_7 + 2H_2O$, crystallises from hot water in orange needles, and decomposes at about 200°, but without melting. The *mercurochloride* (m. p. 272°), *aurochloride* (m. p. 245° with decomposition), *picrate*, and zinc double salt crystallise in yellow needles. The *methiodide*, $C_{17}H_{11}N,MeI$, crystallises from alcohol in brown needles, melts at 237°, and is only sparingly soluble in cold water and insoluble in ether. The corresponding *hydroxide* forms colourless needles, melts at 133°, and is readily soluble in alcohol and ether, but insoluble in water. The *methochloride* crystallises from dilute hydrochloric acid in lustrous needles; its *platinochloride*, $(C_{17}H_{11}N)_2,Me_2PtCl_6$, forms yellow needles.

Phenanthridine and the four bases described above have many properties in common; they are feeble bases, and their salts are all decomposed by water. Their methiodides are decomposed by soda in

the cold, yielding crystalline hydroxides: these compounds are soluble in alcohol and ether, yielding solutions which show a blue and a violet fluorescence respectively, and they form with acids yellow salts, the aqueous solutions of which show a green fluorescence. F. S. K.

Action of Benzoic Acid on Turpentine. By G. Bouchardat and J. Lafont (*Compt. rend.*, **113**, 551—553).—Benzoic acid appears to unite with French turpentine slowly in the cold; at 150°, employing equal weights of acid and turpentine, the action is rapid; after 50 hours' heating, all the turpentine is taken up. The uncombined acid is removed from the product by treatment with an alkali. The portions volatile below 200° separate into solid camphene boiling at 157°, $[\alpha]_D = -3° 30'$, and an isomeric liquid terpilene boiling at 175—180°, $[\alpha]_D = -3°$ to $-4° 30'$. The production of almost inactive camphene and terpilene is accounted for by the formation of turpentine and terpilene benzoates, which, under the prolonged influence of a temperature of 150°, yield acid and camphene and terpilene respectively, hydrocarbons losing their rotatory power rapidly under these conditions. Camphene has been isolated to the extent of 1/10th, and terpilene of 1/3rd, of the weight of the turpentine. The residue left on distilling at 220° forms nearly half the weight of the turpentine. It decomposes on distillation into benzoic acid and camphene hydrocarbons. It may be distilled at 190—195° under a pressure of 30 mm. when a small residue of polyterpilenes remains, consisting principally of colophene, volatile at about 315°. The portion passing over at 190° is an oily mixture of camphenol and isocamphenol benzoates, which are hardly affected by boiling aqueous alkalis, but are hydrolysed in the cold by alcoholic potash; the product of hydrolysis, when washed with tepid water, is partly crystalline. On fractional distillation, lævocamphenol and dextroisocamphenol are separated.

Camphenol, purified by recrystallisation from light petroleum, melts at 193°, and distils at 212°; its rotatory power is $[\alpha]_D = -32° 10'$ to $-32° 20'$. The derived camphor is solid, and has a rotatory power of 38° to 38° 10′. These rotatory powers of the camphenol and camphor are of the same sign, but inferior to those of lævoborneol from Ngai and feverfew camphor. The differences obtain probably owing to the turpentine not being an optically single compound, and, according to the authors' experiments, to the production from the camphene benzoate of inactive or racemic camphenols not separable by solvents from the lævocamphenol. Isocamphenol, purified in the same way, melts at 47°, and boils at 198—199°; its rotatory power is $[\alpha]_D = +10° 40'$ and does not vary under the prolonged action of acids or high temperatures. Phosphorus pentachloride converts isocamphenol, dissolved in light petroleum, into a liquid chloride, which does not solidify even at −60°, boils from 100° to 105° at 40 mm., and is nearly inactive. Nitric acid converts isocamphenol into a liquid substance having the odour of camphor, which, at −60°, forms crystalline plates melting at −20°. This compound, of the same formula as camphor, boils at 13° lower, that is, at about 191°; it is strongly levorotatory. It forms a crystalline compound with hydroxylamine. The properties of this isocamphor assimilate it to the natural

compound, fenolone, obtained by Wallach from essence of fennel, and isocamphenol to the fenolic alcohol derived from it.

The action of benzoic acid at 150° on the turpentines gives a practical method of reproducing camphenols and isocamphenols.

W. T.

Terpenes and their Derivatives. By J. W. Brühl (*Ber.*, **24**, 3373—3416).—The present communication deals exclusively with the constitution and properties of various camphene derivatives.

Menthol is readily converted into cymene by heating it with anhydrous cupric sulphate in sealed tubes for several hours at 250—280°. It is not advisable to use potassium dichromate or potassium permanganate in place of cupric sulphate, since at low temperatures the action of these substances is very feeble, and at higher temperatures violent explosions occur.

Menthyl ethyl ether, $C_{10}H_{19}OEt$, is prepared by boiling menthol (50 grams) dissolved in anhydrous toluene (30 grams) with sodium (8 grams) for 15 hours. The solution is separated from the excess of sodium, and heated with ethyl iodide in excess; the sodium iodide and toluene are removed, and the residue dried and fractionated over sodium in a vacuum. The ether boils at 211·5—212°, under a pressure of 750 mm., and is a colourless liquid, with a slight menthol-like odour.

Bornyl ethyl ether, $C_{10}H_{17}OEt$, is obtained in a manner similar to the preceding compound, xylene being used as a solvent in place of toluene; it is a clear, colourless, viscid liquid, which boils at 97° under a pressure of 20 mm., and at 204—204·5° under a pressure of 750 mm. The yield is 98 per cent. of the borneol employed. All attempts to prepare dibornyl ether were unsuccessful.

Bornyl methylene ether, $CH_2(C_{10}H_{17}O)_2$, is formed by the action of methylene iodide on sodium bornyloxide; it crystallises from light petroleum in colourless, rhombic prisms, melts at 167—168°, and boils under reduced pressure without decomposition; when molten, it exhibits a bluish-yellow fluorescence.

Bornyl methyl ether is formed during the preparation of the preceding compound, and is separated by fractionation.

All attempts to obtain pure sodium camphor have been fruitless. Ethyl camphor, prepared according to Baubigny's method, combines with one atomic proportion of sodium if heated with it in xylene solution, and on treatment with ethyl iodide and subsequent rectification, a viscid liquid is formed, which boils at 156—168° under a pressure of 10 mm., and is probably *diethyl camphor;* it could not be completely purified from lack of material.

The action of sodium on camphor is stated by Baubigny to proceed according to the equation $2C_{10}H_{16}O + 2Na = C_{10}H_{15}NaO + C_{10}H_{17}ONa$; the yield of borneol is, however, considerably less than is indicated by this equation; a portion of the camphor is always recovered unaltered; these facts, as well as the behaviour of the ethereal salts of camphorcarboxylic acid (see below), seem to show that Baubigny's conclusions are incorrect; apparently camphor combines with 2 atoms of sodium, and the reaction which takes place is really represented by the equation $3C_{10}H_{16}O + 4Na = C_{10}H_{14}Na_2O + 2C_{10}H_{17}ONa$.

Camphocarboxylic acid is readily prepared by dissolving camphor (228 grams) in ether (1—1·5 litres), and adding sodium (46 grams) in the form of fine wire; the flask is fitted with a reflux apparatus, and a current of dry carbonic anhydride is passed through the solution; there is considerable development of heat, and the sodium is rapidly dissolved. As soon as the reaction is completed, powdered ice (1 kilo.) is added, the ether separated, and the aqueous solution allowed to remain for 24 hours, when a portion of the borneol separates in crystals, and the remainder is thrown down on heating the filtrate to 50°; the precipitated borneol, after recrystallisation from light petroleum, melts at 208—208·5°; the yield is theoretical. On acidifying the aqueous solution, camphocarboxylic acid is precipitated as a snow-white mass, which, on crystallisation from warm (not boiling) water, yields the pure acid in colourless needles; the yield is almost quantitative. This reaction may be explained by assuming that a disodium salt, $C_8H_{14}<\begin{matrix}C\cdot COONa\\ \|\\ C\cdot O\cdot COONa\end{matrix}$ is first formed, and this, on treatment with water, is decomposed, yielding the compound $C_8H_{14}<\begin{matrix}C\cdot COONa\\ \|\\ C\cdot OH\end{matrix}$, which then by intramolecular change gives sodium camphocarboxylate, $C_8H_{14}<\begin{matrix}CH\cdot COONa\\ \|\\ CO\end{matrix}$. In proof of the foregoing theory, it is found that ethyl camphocarboxylate reacts with sodium and ethyl chlorocarbonate to form a compound, $C_8H_{14}<\begin{matrix}C\cdot COOEt\\ \|\\ C\cdot O\cdot COOEt\end{matrix}$, which on hydrolysis yields camphocarboxylic acid; further, on treating ethyl camphocarboxylate in toluene solution with sodium and carbonic anhydride, and subsequently adding water, the ethereal salt is recovered unchanged, showing that ethyl sodiocamphocarboxylate does not react with carbonic anhydride, or that the compound, if any is formed, is decomposed by water.

Camphocarboxylic acid melts at 127—128°, with evolution of carbonic anhydride. The sodium salt forms a crystalline powder readily soluble in water or dilute alcohol, insoluble in acetone, ether, and carbon bisulphide. The *calcium salt*, $(C_{11}H_{15}O_3)_2Ca$, crystallises from water or alcohol in needles; the *potassium*, *lithium*, and *ammonium* salts resemble the sodium salt. The *ethyl* salt is prepared by dissolving the acid in absolute alcohol, and saturating the solution with hydrogen chloride; it is a colourless, viscid liquid, and boils at 166·8—167·8° under a pressure of 21 mm.; the yield is theoretical.

Sodium acts on ethyl camphocarboxylate, hydrogen being evolved, and on treating the product with ethyl chlorocarbonate, a pale-yellow, viscid liquid, with an odour of pine-apple, is produced; this, after purification, boils at 179·6—181·5° under a pressure of 20 mm. Its physical and chemical properties prove that it has the formula $C_8H_{14}<\begin{matrix}C\cdot COOEt\\ \|\\ CO\cdot COOEt\end{matrix}$ (see above). The author suggests that the ethyl methylcamphocarboxylate," $C_8H_{14}<\begin{matrix}CMe\cdot COOEt\\ \|\\ CO\end{matrix}$, recently

prepared by Minguin, by the mutual action of ethyl camphocarboxylate, methyl iodide, and sodium methoxide, is in reality ethyl camphocarboxylate methyl ether, $C_6H_{14}<\begin{matrix}C\cdot COOEt\\ \|\\ CO\cdot Me\end{matrix}$.

Ethyl camphocarboxylate readily combines with phenylhydrazine when the two are heated together at 100°; the product, after being washed with light petroleum and crystallised from dilute alcohol, is deposited in colourless, slender needles which melt at 132°. It is readily soluble in benzene and chloroform, and the solutions turn red even in the dark; ferric chloride, ammonia, and soda produce a similar change. The substance has the formula $C_{17}H_{20}N_2O + H_2O$, and appears to be a *pyrazolone*, $C_8H_{14}<\begin{matrix}CH\cdot CO\\ |\quad |\\ C:N\cdot NPh\end{matrix}$; it loses 1 mol. H_2O when heated at 100°.

Menthodicarboxylic acid, $C_{10}H_{16}O(COOH)_2$, is prepared in a similar manner to camphocarboxylic acid by the action of carbonic anhydride on menthone (3 mols.) and sodium (4 atoms); the product is treated with ice, in order to decompose the sodium mentholcarbonate, $C_{10}H_{19}O\cdot COONa$, the menthol is extracted with ether, and the aqueous solution, after saturation with sodium chloride, is acidified, and again shaken with ether. On allowing the ethereal solution to evaporate spontaneously, the dicarboxylic acid is obtained in small, colourless prisms; it melts at 128·5° with evolution of carbonic anhydride. It is very unstable, readily dissolves in methyl alcohol and acetone, but only very sparingly in water, chloroform, benzene, or carbon bisulphide. The salts of the alkali metals are exceedingly unstable; the *silver salt* is sparingly soluble, and readily decomposes on exposure to light.

The author discusses the camphor formulæ proposed by Kekulé and by Bredt, and points out that according to the former of these, camphor contains an asymmetric carbon atom; this fact appears to have been generally overlooked, although clearly stated by Van't Hoff.

The formation of a dicarboxylic acid by menthone, and of a monocarboxylic acid by camphor, is probably owing to the presence of the group —$CH_2\cdot CO\cdot CHMe$— in the former compound, whilst the carbonyl group of camphor is only linked to a CH_2 group; menthodicarboxylic acid is therefore represented by the formula

$$CHPr^{\beta}<\begin{matrix}CH_2—CH_2—CMe\cdot COOH\\ CH(COOH)\cdot CO\end{matrix}.$$

Camphoric acid must be regarded as *α-methyl-δ-isopropyl-$\Delta^{\alpha\beta}$-hydromuconic acid*, $COOH\cdot CHPr^{\beta}\cdot CH_2\cdot CH{:}CMe\cdot COOH$, or as a *methyl-isopropyltetramethylenedicarboxylic acid*, $\begin{matrix}CH_2\cdot CPr^{\beta}\cdot COOH\\ |\\ CH_2\cdot CMe\cdot COOH\end{matrix}$, according to whether camphor is represented as having an ethylene linking (Kekulé) or a para-linking. Camphoric acid, which melts at 187°, is not oxidised by potassium permanganate, and is unaffected when heated with anhydrous cupric sulphate under pressure; it is known to be equally stable towards reducing agents and halogen hydrides. The

author confirms Menschutkin's observations on the low etherification value of camphoric acid. Diethyl camphorate is not acted on by bromine at the ordinary temperature, but yields ethyl bromide and camphoric anhydride when heated at 120°. Camphoric anhydride, ethyl chloride, and acetic acid are formed by the action of acetic chloride on ethyl hydrogen camphorate at 100°. All these observations point to camphoric acid as being a tetramethylene derivative, whilst the ease with which it forms the anhydride also tells in favour of its being regarded as a tetra-substituted succinic acid. Further, the hydromuconic acid formula only indicates the existence of three optically isomeric camphoric acids; four, however, are known with certainty, and two others are said to have been isolated; the tetramethylene formula requires six isomerides, four optically active, and two inactive.

The author concludes that camphor can only be accurately represented by the diagonal formula; in other words, he considers that it is derived from a double tetramethylene ring, $\begin{matrix}CH_2\cdot CH\cdot CH_2\\ | \quad | \quad |\\ CH_2\cdot CH\cdot CH_2\end{matrix}$.

J. B. T.

German and Turkish Rose-oil. By U. Eckart (*Arch. Pharm.*, **229**, 355—389).—Rose-oil consists of ethyl alcohol, which is distilled off below 100° and constitutes 5 per cent. of the oil, the elæoptene, which constitutes practically the whole of the liquid portion of the oil, and the stearoptene, which is the solid portion. The two latter are separated by dissolving the oil in 75 per cent. alcohol at 70—80°, and cooling to 0°, when the stearoptene separates; the alcoholic solution is then evaporated in a vacuum to obtain the elæoptene.

The elæoptene, from both Turkish and German rose-oil, has a composition corresponding with the formula $C_{10}H_{18}O$. Its physical constants vary, according to its source, between the following limits:—Boiling point, 216—217°; refractive index, 1·4710—1·4725; refraction equivalent, 48·97—49·28; dispersion 11·1—12·5; specific rotation, −2·7 to −2·8. The vapour density corresponds with the molecular weight 142·43 ($C_{10}H_{18}O$ = 154). Evidence of Markovnikoff's compound $C_{10}H_{20}O$ (Abstr., 1891, 219) was not obtained.

The author proposes the name *rhodinol* for the compound $C_{10}H_{18}O$. The following derivatives of it are described:—The *sodium* derivative, not prepared perfectly pure; the *chloride*, $C_{10}H_{17}Cl$, a yellowish-brown liquid which does not distil without decomposition; the *iodide*, $C_{10}H_{17}I$, a brown liquid with an odour of turpentine; the *cyanide*, a yellow oil. The *ether*, $C_{20}H_{34}O$, was obtained by acting on rhodinol with carbanil, whereby a crystalline *carbanilide* melting at 235° was formed; this was subsequently decomposed by water, when the ether separated as a yellow liquid. The *benzoate*, $PhCOO\cdot C_{10}H_{17}$, is a pale-yellow neutral liquid; the *acetate*, $MeCOO\cdot C_{10}H_{17}$, and the *thio-alcohol*, $C_{10}H_{17}\cdot SH$, were also obtained.

By oxidising rhodinol with potassium dichromate and sulphuric acid, the corresponding *rhodinaldehyde*, $C_{10}H_{16}O$, and the *silver* salt of the *acid*, $C_{10}H_{16}O_2$, *rhodinolic acid*, were prepared. When alkaline permanganate was used as the oxidising agent, a pentahydric

alcohol, $C_6H_{14}O_5$, and the following acids were obtained:—Valeric, butyric, acetic, formic, oxalic, and carbonic. When hydrogen peroxide was used, a monobasic *acid*, $C_6H_{12}O_6$, was formed, of which the *barium* salt, $(C_6H_{11}O_2)_2Ba$, was analysed.

Strong dehydrating agents act on rhodinol to form a hydrocarbon of the limonene group, namely, dipentene, $C_{10}H_{16}$, and a polyterpene, $(C_5H_8)_n$.

The stearoptene is colourless and odourless; its quantity varies in rose-oil between 20 and 68 per cent., and its melting point between 33·5° and 36·5°.

The author regards rhodinol as an unsaturated monhydric primary alcohol with an open-chain structure. Its optical activity shows the presence of an asymmetrical carbon atom, and by applying Brühl's method to the refraction equivalent, it would appear to contain two ethylenic linkings; the author therefore attributes to it the formula $CH_2{:}CPr{\cdot}CH{:}CH{\cdot}CHPr{\cdot}CH_2{\cdot}OH$, which would also account for its easy conversion into closed-chain compounds (compare Semmler, Abstr., 1890, 951). A. G. B.

Natural Resins. By M. Bamberger (*Monatsh.*, **12**, 441—463).—The resin from *Pinus laricio* (Poir) dissolves in alcohol, ether, methyl alcohol, amyl alcohol, acetone, and acetic acid; is partly soluble in benzene, chloroform, and turpentine, and is insoluble in light petroleum. It melts at about 100°; has a yellow colour which, on exposure to light becomes red, gives the phloroglucinol reaction, and, on distillation in a vacuum, furnishes a viscid, brown mass. As determined by Schmidt and Erban's method (*Monatsh.*, **7**, 655), the specimens examined had an acid equivalent of 116·6 and an iodine number of 51·9. The methoxyl number obtained by Benedikt and Grüssner's process varied from 49·6 to 54·8.

On boiling with water for a long time, or on blowing steam through an alcoholic solution, and exhausting with ether, the ethereal solution obtained gave, on evaporation, a crystalline mass which had an iodine number of 60·4. This was dissolved in alcohol, and allowed to crystallise. The first separation consisted of caffeïc acid, the diacetyl derivative of which formed slender, white needles, melted at 189°, and agreed in properties with the compound obtained by Tiemann and Nagai (*Ber.*, **11**, 656), who, however, give a slightly higher melting point, namely, 190—191°. On reduction of the acid with sodium amalgam, hydrocaffeïc acid, $C_9H_{10}O_4$, identical in crystalline [$a : b : c$ form = 2·5604 : 1 : 1·9676, $\eta = 108°$] and optical properties with the acid obtained by Hlasiwetz (*Annalen*, **142**, 354), was formed. The second separation was recrystallised from chloroform and from hot water, and proved to be ferulic acid. The mother liquor was then evaporated to dryness, dissolved in ether, the solution shaken with bisulphite, and finally treated in the way recommended by Tiemann (*Ber.*, **8**, 115), whereby vanillin was obtained.

On heating the resin (500 grams) left after boiling with water, with potash (2 kilos.) in an iron dish, a mixture of catechol and protocatechuic acid was obtained. Of these substances, the former is

probably derived from the latter, and the latter from ferulic acid, by the action of potash.

The resin from *Picea vulgaris* (Link) melts at about 100°, and the samples examined had an acid equivalent of 125—127·7, an iodine number of 61·2, and a methoxyl number of 33—34·9. The resin was treated in the same way as that obtained from *Pinus laricio*, and gave an aqueous extract which contained paracoumaric (naringenic) acid and vanillin. The resin, after boiling with water, had an acid equivalent of 99 and a methoxyl number of 34·8; and gave, on fusion with potash, a mixture of protocatechuic and parahydroxybenzoic acids.

G. T. M.

Substances contained in the Petals of Gentiana verna. By G. Goldschmiedt and R. Jahoda (*Monatsh.*, **12**, 479—485).—On evaporation of an alcoholic extract of 1 kilo. of the air-dried petals of *Gentiana verna*, a dark-red, viscid mass, containing solid, greenish-yellow, resinous lumps, is obtained. Water dissolves a reddish-violet colouring matter, dextrose, levulose, and another substance from the product, and leaves the resinous lumps unchanged. The resin dissolves in alcohol, and after treatment with charcoal forms a colourless solution from which three compounds may be separated by fractional crystallisation. That formed in greatest quantity is an amorphous, granular, white powder which melts at 215—219°. Elementary analysis and a determination of its effect in lowering the freezing point of phenol show that it has the formula $C_{30}H_{48}O_3$. It is without action on hydroxylamine and phenylhydrazine, but forms a triacetyl derivative, $C_{30}H_{45}(OAc)_3$, which is readily soluble in cold alcohol and melts at 175—180°, and, consequently, contains three hydroxyl groups, and has been named *gentiol* by the authors. It is readily soluble in hot alcohol, dissolves sparingly in ether and benzene, is insoluble in potash, and, on oxidation with chromic acid in acetic acid solution, gives a crystalline acid which melts at 127°. The two other fractions are only obtained in small quantity; one is soluble in alcohol, ether, and benzene, crystallises in beautiful, white plates, melts at 115—117°, and has the formula $C_{38}H_{64}O_3$; the other is a yellowish powder, which melts at about 240°. G. T. M.

Rind of Garcinia Mangostana. By P. R. Liechti (*Arch. Pharm.*, **229**, 426—439).—The author fully describes his method of preparing mangostin from the rind of *Garcinia mangostana;* it does not materially differ from that adopted by Schmid (*Annalen*, **93**, 83; *J. Chem. Soc.*, 1856, 190).

Pure mangostin, $C_{20}H_{22}O_5$, crystallises in bright-yellow, slender laminæ, melts at 173° (uncorr.), not at 190° (Schmid, *loc. cit.*), and is tasteless and odourless; it dissolves with a yellow colour in alcohol, ether, chloroform, glacial acetic acid, carbon bisulphide, xylene, acetone, strong sulphuric acid, and alkalis; it is sparingly soluble in benzene and solution of tannin, but not at all in light petroleum. Solutions of mangostin give a greenish-black colour with ferric chloride. Alkaline solutions of it fluoresce greenish, dissolve ferric hydroxide with a deep red-brown colour, and give an orange preci-

pitate with alkaline potassium iodide. Gold, silver, and platinum are reduced from their solutions by mangostin.

Mangostin is oxidised by nitric acid to oxalic acid. When it is heated with potassium hydroxide and a little water until the melt has a clear brown colour, and the melt subsequently dissolved in water, acidified, and extracted with ether, a small quantity of acid, resembling valeric acid in its odour and in its zinc salt, is obtained; if the melt is more strongly heated, carbonic anhydride and oxalic acid are produced.

When mangostin is reduced in alcoholic solution with sodium amalgam, and the solution filtered and acidified, a brick-red, amorphous precipitate is obtained which dissolves in alcohol; the solution gives a briliiant, green fluorescence when mixed with a little alkali. The absorption spectrum of this fluorescent solution contains a strong band between E and *b*, and a feeble band at F. This reduction product has the same percentage composition as mangostin, and is called *isomangostin* by the author, who regards it as a polymeride. It melts with partial decomposition at 127° (uncorr.); its solutions in alcohol and in ether are yellowish-brown, and are not further coloured by ferric chloride, nor will they reduce ammoniacal silver solution.

Schmid (*loc. cit.*) found that gamboge yielded a substance closely resembling mangostin when oxidised by nitric acid. The author prepared pure gambodic acid from gamboge by dissolving in absolute alcohol, filtering, precipitating with water, washing, dissolving in dilute ammonia, and precipitating with hydrochloric acid; it melts at 92—96° (uncorr.). This preparation was oxidised with nitric acid, and the product analysed; but in its composition and properties it bore no resemblance to mangostin.

Mangostin gives a white, crystalline acetate with acetic anhydride and sodium acetate, which is being investigated.

Some remarks on the anatomy of the rind of *Garcinia mangostana* conclude this paper. A. G. B.

Nicotenylamidoxime. By L. Michaelis (*Ber.*, **24**, 3439—3446). —*Nicotenylamidoxime*, $C_5NH_4{\cdot}C(NH_2){:}N{\cdot}OH$, is prepared by digesting equivalent quantities of β-cyanopyridine, hydroxylamine hydrochloride, and sodium carbonate in concentrated aqueous solution for eight hours at 70° in a closed vessel. The mixture is evaporated to dryness, extracted with absolute alcohol, the alcohol distilled off, and the product crystallised from hot chloroform. It melts at 128° without decomposition, is easily soluble in water, alcohol, acetone, alkalis, and acids, sparingly so in ether, chloroform, and benzene, and insoluble in light petroleum. With ferric chloride, it gives a red coloration; with Fehling's solution, a dirty brownish-green precipitate. The *hydrochloride*, $C_6H_7N_3O,2HCl$, is prepared by leading dry hydrogen chloride into a dry ethereal solution of the amidoxime. It forms very deliquescent needles, melts at 171°, and is soluble in water and alcohol. The *platinochloride* obtained by adding platinic chloride to a concentrated solution of the hydrochloride, crystallises in yellow scales, and is soluble in water and alcohol. Stannic chloride and

mercuric chloride cause no precipitate when added to an aqueous solution of the hydrochloride. The *copper* salt is obtained by adding copper acetate to an aqueous solution of the ammonium salt, and is soluble in ammonia and hydrochloric acid, insoluble in water. The *silver* salt is white, and blackens in the air.

Acetylnicotenylamidoxime, $C_5NH_4{\cdot}C(NH_2){:}NOAc$, is formed with development of heat on mixing finely-powdered nicotenylamidoxime with acetic anhydride. When the reaction is ended, the product is neutralised with sodium carbonate, filtered, and purified by crystallisation from chloroform. It melts at 143°, and is easily soluble in benzene, alcohol, acetone, chloroform, and acids, less so in water, ether, and light petroleum.

Nicotenylazoximethenyl, $C_5NH_4{\cdot}C\begin{matrix}NO\\ \diagdown\!\diagup\\ N\end{matrix}CMe$, is obtained as a sublimate by cautiously heating the preceding compound between watch-glasses on the sand-bath. It melts at 109°, and is soluble in water, ether, alcohol, benzene, acetone, chloroform, and acids, insoluble in alkalis. The *hydrochloride* forms small, white needles, and is soluble in water and alcohol. The *platinochloride* is obtained in beautiful yellow needles on adding platinic chloride to a solution of the hydrochloride, and is sparingly soluble in water, insoluble in alcohol. Mercuric chloride gives a white precipitate when added to a concentrated solution of the hydrochloride. Stannic chloride gives no precipitate.

Benzoylnicotenylamidoxime, $C_5NH_4{\cdot}C(NH_2){:}NO{\cdot}Bz$, is prepared by adding the calculated quantity of benzoic chloride to nicotenylamidoxime dissolved in the calculated quantity of sodium hydroxide. The mixture is shaken as long as the odour of benzoic chloride can be detected, a few drops of ammonia added, and the compound collected, washed with water, and crystallised from alcohol. It forms colourless scales, melts at 190°, is easily soluble in benzene, alcohol, and chloroform, very sparingly in ether and water, and insoluble in light petroleum. It dissolves in acids, and is reprecipitated by alkalis.

Nicotenylazoximebenzenyl, $C_5NH_4{\cdot}C\begin{matrix}NO\\ \diagdown\!\diagup\\ N\end{matrix}CPh$, is obtained as a sublimate by heating the preceding compound between watch-glasses or by boiling it for a long time with water. It melts at 139°, and is soluble in ether, benzene, light petroleum, alcohol, acetone, chloroform, and acids, and insoluble in water and alkalis. The *hydrochloride* is unstable. With platinic chloride and mercuric chloride, it yields sparingly soluble double salts.

Nicotenylazoximepropenyl-ω-carbonic acid,

$$C_5NH_4{\cdot}C\begin{matrix}NO\\ \diagdown\!\diagup\\ N\end{matrix}C{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained by heating a mixture of molecular proportions of nicotenylamidoxime and succinic anhydride at 100° to quiet fusion. The cold mass is extracted with dilute soda, filtered, and the filtrate saturated with dilute hydrochloric acid. The compound is obtained as a voluminous precipitate, and is purified by crystallisation from hot

water. It melts at 178°, is soluble in water, acetone, alcohol, acids, and alkalis, sparingly so in ether, chloroform, and benzene, insoluble in light petroleum, and reacts acid to litmus. The *silver* salt forms stellate groups of needles, blackens on exposure to light, and is soluble in ammonia. The *copper* salt is green, and dissolves in ammonia to a blue solution.

Nicotenylphenyluramidoxime, $C_5NH_4{\cdot}C(:NOH){\cdot}NH{\cdot}CO{\cdot}NHPh$, is obtained by mixing finely-divided nicotenylamidoxime with the calculated quantity of carbanil. It crystallises from chloroform in slender needles, melts at 167°, is easily soluble in hot water, alcohol, and chloroform, less so in benzene, ether, and acetone, and insoluble in light petroleum, acids and alkalis.

Ethyl nicotenylamidoximecarbonate, $C_5NH_4{\cdot}C(NH_2):NO{\cdot}COOEt$, is formed together with nicotenylamidoxime hydrochloride by adding ethyl chlorocarbonate (2 mols.) drop by drop to a saturated solution of nicotenylamidoxime (3 mols.) in absolute ether. It is purified by dissolving in benzene and precipitating with petroleum, melts at 136° and is soluble in water, alcohol, benzene, chloroform, acetone, and acids, insoluble in ether and light petroleum.

Nicotenylazosulphimecarbanilide, $C_5NH_4{\cdot}C\begin{matrix}<^{NS}\\ >_{N}\end{matrix}C{\cdot}NHPh$, is obtained on gently warming a mixture of finely-powdered nicotenylamidoxime and phenylthiocarbimide. The reaction takes place suddenly with much frothing, and the product is purified by several crystallisations from hot benzene. Although the experimental conditions were varied, the author could not obtain a nicotenylthiouramidoxime, but always obtained the condensation product. Nicotenylazosulphimecarbanilide is also obtained on heating to boiling nicotenylamidoxime (1 mol.) and phenylthiocarbimide (2 mols.) dissolved in chloroform. It crystallises in white needles, melts at 241°, is insoluble in water, soluble in alcohol, benzene, and chloroform, less so in ether and acetone, and is dissolved by acids and reprecipitated by alkalis.

Nicotenylamidoxime benzyl ether, $C_5NH_4{\cdot}C(NH_2):NO{\cdot}CH_2Ph$, is obtained by gently heating equivalent quantities of nicotenylamidoxime, sodium ethoxide, alcohol, and benzyl chloride in a reflux apparatus. It crystallises from light petroleum in needles, melts at 80°, is soluble in ether, alcohol, benzene, chloroform, and petroleum, insoluble in water, and dissolves in acids, but not in alkalis. E. C. R.

α-Pyridone (α-Hydroxypyridine). By H. v. Pechmann and O. Baltzer (*Ber.*, **24**, 3144—3153).—To prepare α-pyridone (α-hydroxypyridine), malic acid (500 grams) is converted into cumalic acid by heating it with sulphuric acid, and thence into the methyl salt; this is dissolved in ammonia, and boiled with sodium hydroxide, and on then adding hydrochloric acid, hydroxynicotinic acid is precipitated, which is dried and heated above its melting point until the evolution of carbonic anhydride slackens, when the temperature is raised and α-pyridone passes over. It melts at 107°, boils at 280—281°; the aqueous solution has a neutral reaction; the colour produced by ferric chloride is quite distinct from that obtained with phenol, and the observation that both the ethyl derivatives (see below) give the same

colour stands in harmony with this difference; it does not give Liebermann's phenyl reaction, and does not, under any circumstances, reduce permanganate solution instantaneously; when mercuric chloride is added to a concentrated solution, the *mercurochloride* separates, and this on crystallisation from water or dilute alcohol, forms long, colourless needles, and melts at 191—192°.

Ethyl-α-pyridone is obtained in theoretical yield by heating α-pyridone with an excess of ethyl iodide for five hours at 180°, adding hydrochloric acid, evaporating on the water-bath, redissolving in a little water, precipitating with an excess of potassium carbonate, extracting with chloroform, and rectifying. It is a colourless, almost odourless oil of strong basic properties, boils at 246—248°, is very sparingly volatile with steam, is miscible with water, and when heated at 290° in a sealed tube, undergoes partial decomposition, the residue being the unaltered compound; it behaves towards permanganate in a manner similar to α-pyridone; the *mercurochloride* crystallises from water or dilute alcohol in prisms, and melts at 112—113°; the *hydrochloride* is completely volatilised by protracted heating at the temperature of the water-bath; the *platinochloride* forms yellow needles, sinters at 98°, and melts at 105—108°. When ethyl-α-pyridone is heated in a reflux apparatus with an excess of 4 per cent. sodium amalgam, ethylamine is produced; the authors, therefore, believe it to have the constitution $CH\ll^{CH\cdot CO}_{CH:CH}\gg NEt$.

α-Ethoxypyridine is formed by shaking silver α-pyridone (prepared by adding the calculated quantity of silver nitrate to α-pyridone dissolved in the equivalent quantity of dilute soda) with ether and ethyl iodide at the ordinary temperature, until the precipitate has the colour of silver iodide, filtering, washing the precipitate with alcoholic hydrochloric acid, distilling off the alcohol and ether, mixing the residue with a little water, and precipitating the base with potassium carbonate; the yield is equal to the α-pyridone employed. It is a colourless oil, having a strong odour of pyridine and more feeble basic properties than its isomeride; it boils at 155—156°, is volatile with steam, and is much more stable than its isomeride, remaining unchanged when heated in a sealed tube at 230°, and being only very slowly attacked at the ordinary temperature by permanganate; the *mercurochloride* melts at 141—142°. When heated in dilute alcoholic solution with sodium amalgam, ammonia is evolved; it, therefore, probably has the constitution $CH\ll^{CH\cdot C(OEt)}_{CH=\!=CH}\gg N$.

Methyl-α-pyridone, C_5NH_4MeO, is a colourless, almost odourless liquid boiling at 240°; the *mercurochloride* melts at 127°.

α-Methoxypyridine, $C_5NH_4\cdot OMe$, closely resembles the ethyl derivative; the mercurochloride melts at 199—200°.

α-Chloropyridine [Cl = 2] is obtained by moistening α-pyridone with phosphorus oxychloride, mixing with $2\frac{1}{2}$ times the quantity of phosphorus pentachloride, and heating the mixture for 3—4 hours in an oil-bath at 130°, adding water, and after rendering alkaline, driving over the new base with steam; it is a colourless oil having a pyridine-like odour, boils at 166° (714 mm.), and is insoluble in

water; the *platinochloride* crystallises in the monosymmetric system, $a : b : c = 1{\cdot}4348 : 1 : 2{\cdot}0380$; $\beta = 73^{\circ}\ 21{\cdot}4'$; observed forms ∞P, $-\text{P}\infty$, 0P.

The concluding portion of the paper is devoted to a discussion on the constitution of pyridine by v. Pechmann, who considers that the general behaviour of pyridine, including the tautomerism of its hydroxy-derivatives (see also Haitinger and Lieben, Abstr., 1885, 966), is best explained by assigning to it a centric formula as suggested by Bamberger. A. R. L.

Piperazine. By A. Schmidt and G. Wichmann (*Ber.*, **24**, 3237—3248).—Majert and Schmidt (Abstr., 1891, 538) have already stated that piperazine passes unchanged through the human organism. The authors find that with a single dose of 3 grams the base can be detected in the urine even after 6 days, and although the chief portion is voided after a few hours, a certain amount remains in the blood for a long period. To detect piperazine in urine, the latter is rendered free from phosphates of the earth-metals by the addition of a few drops of sodium hydroxide solution, reacidified with hydrochloric acid, heated to 40°, and filtered after the addition of a solution of potassium bismuthoiodide, when crystals of the form already described (*loc. cit.*) separate from the filtrate after a time. In the detection of minute quantities of the base, the urine is evaporated, the residue being distilled with solid alkali and sand, and the distillate examined as above. Piperazine undergoes no change when directly injected into the blood, for example; by injecting 0·3 gram into the blood of a rabbit, the chief portion was found in the urine after 2 hours, but the presence of the base could still be detected at the end of $1\frac{1}{2}$ days.

When dry piperazine (1 gram) is heated for 14 hours at 270° with bromobenzene (11 grams), the product filtered from bromide, and distilled until the thermometer registers a temperature of 170°, alcohol extracts diphenylpiperazine (m. p. 160°) from the residue. Piperazine (8 grams) and bromobenzene (3 grams) heated in a similar manner give the same compound together with an oily substance, probably monophenylpiperazine.

Paranitrophenylpiperazine, $NO_2{\cdot}C_6H_4{\cdot}C_4H_9N_2$, is obtained when piperazine (8 grams) is heated with parachloronitrobenzene (3 grams) at 150° for 4 hours; the melt is triturated with dilute alkali, and the residue extracted with hydrochloric acid, when a small quantity of dinitro-derivative (see below) remains undissolved, together with chloronitrobenzene; the filtrate is freed from chloronitrobenzene by agitating it with ether, alkali added, and the precipitate which forms is dissolved in benzene; the pure compound separates from this solution on adding light petroleum; it melts at 129°, and is readily soluble in alcohol, chloroform, and benzene, but only very sparingly in water, ether, and light petroleum; the *hydrochloride* forms yellowish-red, lustrous prisms. *Paradinitrodiphenylpiperazine*,

$$C_4H_8N_2(C_6H_4{\cdot}NO_2)_2,$$

is almost exclusively formed when the previously mentioned re-

agents are heated together, in molecular proportion, for 3 hours at 150°; the product, after washing with water, is treated with boiling alcohol, when the dinitro-compound remains; it is very sparingly soluble in all solvents and melts at 248° with decomposition. *Diacetylpiperazine*, $C_4H_8N_2Ac_2$, is prepared by heating piperazine acetate with an excess of acetic anhydride in a reflux apparatus, distilling off to 300°, rectifying the residue in a vacuum, and crystallising the solidified distillate from benzene, when the compound separates in compact needles; it melts at 138·5°, boils with slight decomposition at 310°, and is readily soluble in water and alcohol. *Ethyl piperazyloxamate*, $C_4H_8N_2(CO{\cdot}COOEt)_2$, is formed when piperazine is heated at 100° for a short time with an excess of ethyl oxalate; it crystallises from water in needles, melts at 124°, and is readily soluble in solvents.

The *compound* $C_4H_{10}N_2,2PhOH$, which separates on mixing an alcoholic solution of piperazine with an ethereal solution of phenol in molecular proportion, crystallises from alcohol in large, lustrous prisms, melts at 99—101°, and develops the odour of phenol on keeping; whilst the *compound*, $C_4H_{10}N_2,C_6H_6O_2$, melting at 195°, with decomposition, separates in compact needles on mixing alcoholic solutions of piperazine and quinol.

The *benzylidene derivative*, $C_4H_8N_2{\cdot}CHPh$, produced by mixing piperazine with benzaldedyde, heating on the water-bath, and treating with boiling alcohol, is a white, amorphous substance almost insoluble in all solvents, and melts at 246—247°; whilst the compound $C_4H_{10}N_2CS_2$ separates as a greenish-white powder, on mixing alcoholic solutions of piperazine and carbon bisulphide; it decomposes at 260°.

Diazobenzenepiperazine, $C_4H_8N_2(N_2Ph)_2$, prepared by adding piperazine to an alkaline solution of diazobenzene, melts at 129°; a compound is also obtained with quinone.

Dichloropiperazine, $C_4H_8N_2Cl_2$, is best prepared by adding an aqueous solution of piperazine to one of freshly prepared sodium hypochlorite, collecting the precipitate and crystallising it from alcoholic ether; it has a sharp, tear-exciting odour, melts at 71°, detonates at 80—85°, is sparingly soluble in water, but is converted into piperazine hydrochloride by it, only slightly soluble in ether, and readily in alcohol. No analogous compound is formed by the action of sodium hypobromite, although the addition of bromine water to an aqueous solution of piperazine seems to produce it.

Dinitrosopiperazine (Ladenburg, Abstr., 1891, 1333) decomposes when distilled, and, on reduction with zinc and acetic acid, yields the *dihydrazine*, $C_4H_8N_2(NH_2)_2$, crystallising from alcoholic either in stout needles, melting at 100°, and boiling at 228°; the latter reduces Fehling's solution and ammoniacal silver solution on boiling; the *dibenzoyl derivative*, $C_4H_8N_2(NHBz)_2$, prepared by adding the calculated quantity of benzoic chloride dissolved in chloroform to a solution of the hydrazine in the same solvent, is a white, amorphous substance which does not melt at 310°, and is insoluble in solvents; whilst the *dibenzylidene derivative*, $C_4H_8N_2(N{\cdot}CHPh)_2$, obtained by adding benzaldehyde to a solution of the hydrazine in sodium acetate solution, melts at 205°, and is insoluble in water.

Dimethylpiperazine (Ladenburg, *loc. cit.*) boils at 153—158°, and does not solidify when cooled to −15°; the hydrochloride melts at 247—250° with decomposition. *Diethylpiperazine*, $C_4H_8N_2Et_2$, boils at 165°, and does not solidify at −15°; the *hydrochloride* crystallises from dilute alcohol in small, white needles, melts at 277° with decomposition; the *platinochloride* forms small, yellow plates.

A. R. L.

Quinolinehydrazines. By E. Böttiger (*Ber.*, **24**, 3276—3277). —A claim for priority. Dufton's researches on orthoquinolinehydrazine (Trans., 1891, 752) were not published until October, whereas the author had already, in August, applied for a patent concerning a method of preparation of quinolinehydrazines. He thinks he has at least an equal right with Dufton to be regarded as the discoverer of these compounds.

C. F. B.

μ-Phenylpentoxazoline. By S. Gabriel and P. Elfeldt (*Ber.*, **24**, 3213—3218).—The benzoyl derivative of γ-bromopropylamine, like the benzoyl derivatives of β-bromethylamine and β-bromopropylamine (Abstr., 1890, 1267), readily loses hydrogen bromide, forming a meso-substituted pentoxazoline,

$$CH_2<\begin{matrix}CH_2\cdot O\\CH_2\cdot N\end{matrix}>CPh,$$

which contains the same nucleus as trimethylenepseudocarbamide (Abstr., 1890, 472). The γ-bromopropylamine required was prepared according to Gabriel and Weiner's method (Abstr., 1888, 1292), and was freed from admixed trimethylenediamine hydrobromide by solution in absolute alcohol. The crude compound obtained on evaporating the solution was dissolved in water and treated with 2 mols. of sodium carbonate and 1 mol. of benzoic chloride; *γ-bromopropylbenzamide*, $CH_2Br\cdot CH_2\cdot CH_2\cdot NH\cdot COPh$, then separates as a white, crystalline compound, which is purified by triturating with dilute soda and recrystallising from benzene. It forms white, fascicular groups of needles melting at 62°. The crystals deliquesce in the course of a few weeks, and pass into the hydrobromide of *μ-phenylpentoxazoline*, $CH_2<\begin{matrix}CH_2\cdot O\\CH_2\cdot N\end{matrix}>CPh$; the free base separates on the addition of soda. It may be more quickly prepared by dissolving the benzamide in hot water, adding alkali, distilling in a current of steam, and extracting the distillate with ether. On evaporating the latter, the μ-phenylpentoxazoline remains as a yellowish oil, having a peculiar odour and pungent taste; it is sparingly soluble in cold, more readily in hot, water, and cannot be distilled under atmospheric pressure without decomposition. The *picrate*,

$$C_{19}H_{11}NO,C_6H_3N_3O_7,$$

forms yellow needles and melts at 151°; the *platinochloride*, orange-yellow, flat needles melting with decomposition at 185°; the *dichromate*, orange needles; and the *ferrocyanide*, a yellowish-green, crystalline precipitate.

Towards hot mineral acids the base behaves in a manner similar to the oxazoline bases previously described; with an excess of hydrobromic acid, it is reconverted into γ-bromopropylbenzamide, and with an excess of hydrochloric acid into *γ-chloropropylbenzamide*,

$$CH_2Cl\cdot CH_2\cdot CH_2\cdot NH\cdot COPh,$$

which crystallises from light petroleum in delicate needles, melts at 56—57°, and is much more stable than the bromine derivative. If, however, the base be boiled with an equivalent quantity of aqueous hydrobromic acid until the solution no longer forms a sparingly soluble dichromate, it is converted into the *hydrobromide* of *γ-amidopropyl benzoate*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OBz$, which separates from acetic acid, on the addition of ethyl acetate, as a white, crystalline powder, melts at 134—135°, is readily soluble in water, and sparingly in light petroleum. The free *γ-amidopropyl benzoate* is a colourless oil easily soluble in water; its *picrate*, $C_{10}H_{13}NO_2,C_6H_3N_3O_7$, crystallises in yellow needles, and melts at 177—178°, and the *platinochloride*, $(C_{10}H_{13}NO_2)_2,H_2PtCl_6$, in yellowish-red needles melting with decomposition at 204—205°.

Corresponding with pentoxazoline is the compound pentathiazoline; this has not yet been prepared, but some of its derivatives are already known, namely, μ-mercaptopenthiazoline, $C_3H_6{<}\overset{S}{\underset{N}{>}}C\cdot SH$, and trimethylenepseudothiocarbamide (Abstr., 1890, 524). Other derivatives have been obtained by the action of trimethylene bromide on thioamides, and will shortly be described. H. G. C.

Oxazolines and Pentoxazolines. By P. Elfeldt (*Ber.*, **24**, 3218—3228).—In continuation of the work described in the previous abstract, the author has examined other derivatives of bromethylamine and bromopropylamine, and finds that these, like the acetyl and benzoyl compounds, readily yield oxazolines and pentoxazolines.

Metanitrobenzoic chloride acts on β-bromethylamine in presence of sodium carbonate, forming *β-bromethylmetanitrobenzamide*,

$$CH_2Br\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

which crystallises in needles melting at 116—117°, and is almost insoluble in cold water. It is converted by the calculated quantity of alcoholic potash into *μ-metanitrophenyloxazoline*,

$$\begin{matrix}CH_2\cdot O\\ |\\ CH_2\cdot N\end{matrix}{>}C\cdot C_6H_4\cdot NO_2,$$

which crystallises from water or dilute alcohol in long, narrow, rectangular plates melting at 118·5—119·5°. Of its salts, the *picrate*, $C_9H_8N_2O_3,C_6H_3N_3O_7$, melts at 145—146°, and the *platinochloride*, $(C_9H_8N_2O_3)_2,H_2PtCl_6$, at 195°; the *dichromate* forms a yellowish-red emulsion, and the *ferrocyanide* a yellowish-green, crystalline precipitate.

β-Bromopropylamine hydrobromide (which, after recrystallisation from acetic acid, melts at 156°) is readily acted on by metanitrobenzoic chloride and alkali, with formation of *β-bromopropylmetanitrobenz-*

amide, $CHMeBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, which crystallises from benzene in small needles melting at 84—85°, and is converted by alcoholic potash into *β-methyl-μ-metanitrophenyloxazoline*,

$$\begin{matrix} CHMe{\cdot}O \\ | \\ CH_2{-}N \end{matrix}\!\!>\!C{\cdot}C_6H_4{\cdot}NO_2.$$

This crystallises from water or dilute alcohol in long, silvery plates, melts at 85—86°, and is only slightly volatile in a current of steam; its *picrate*, $C_{10}H_{10}N_2O_3,C_6H_3N_3O_7$, crystallises in yellow needles, and melts at 152—153°, and the *platinochloride*, $(C_{10}H_{10}N_2O_3)_2,H_2PtCl_6$, forms flat, yellowish-red, quadratic crystals melting at 195—196° with decomposition.

γ-Bromopropylaminenitrobenzamide is obtained in a manner similar to the *β*-compound, and crystallises from benzene or chloroform in needles melting at 89—90°; by the action of alcoholic potash, it yields *μ-metanitrophenylpentoxazoline*, $CH_2\!<\!\begin{matrix} CH_2{\cdot}O \\ | \\ CH_2{\cdot}N \end{matrix}\!\!>\!C{\cdot}C_6H_4{\cdot}NO_2$, which separates from dilute alcohol or ether in long, silvery plates melting at 93—94°. The *picrate*, $C_{10}H_{10}N_2O_3,C_6H_3N_3O_7$, crystallises in tufts of needles, and melts at 123—124°, previously becoming plastic, and the *platinochloride*, $(C_{10}H_{10}N_2O_3),H_2PtCl_6$, forms an orange-red, crystalline powder which melts with decomposition at 196°.

β-Bromethylphenylacetamide, $C_2H_4Br{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, obtained from phenylacetic chloride and *β*-bromethylamine hydrobromide, crystallises from benzene in small, jagged plates, and melts at 84—85°. When treated with aqueous soda and distilled in a current of steam, it yields *μ-benzyloxazoline*, $\begin{matrix} CH_2{\cdot}O \\ | \\ CH_2{\cdot}N \end{matrix}\!\!>\!C{\cdot}CH_2Ph$, which may be extracted from the distillate with ether, and remains, on evaporating the solvent, as an oil having a feeble, penetrating odour. The *picrate*, $C_{10}H_{11}NO,C_6H_3N_3O_7$, melts at 130—131°. The larger quantity of the phenylacetamide is, however, converted into *amidoethyl phenylacetate hydrobromide*, $NH_2{\cdot}C_2H_4{\cdot}O{\cdot}CO{\cdot}CH_2Ph,HBr$, which is isolated by evaporating the solution of the amide to dryness, extracting the residue with water, and slowly evaporating the solution. The residue probably contains hydroxyethylamine hydrobromide, and is therefore treated with picric acid, which does not precipitate the latter, but yields the *picrate* of amidoethyl phenylacetate in small plates melting at 137—138°.

Phenylacetic chloride reacts with *β*-bromopropylamine much less readily than with the corresponding ethyl derivative; the *β-bromopropyl phenylacetamide*, $CHMeBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, crystallises from light petroleum in delicate needles, melts at 45—46°, and when kept rapidly forms a syrup, which is partially soluble in water. The solution gives precipitates with picric acid and platinum chloride, the former having the composition $C_{11}H_{13}NO,C_6H_3N_3O_7$; the solution, therefore, in all probability contains *β-methyl-μ-benzyloxazoline*, $\begin{matrix} CHMe{\cdot}O \\ | \\ CH_2{-}N \end{matrix}\!\!>\!C{\cdot}CH_2Ph.$

γ-Bromopropylphenylacetamide, $C_3H_6Br{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, separates from light petroleum in tufts of slender needles, melts at 43—44°, and decomposes if kept, or by the action of alkalis, forming *μ-benzylpentoxazoline*, $CH_2<\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}N\end{matrix}>C{\cdot}CH_2Ph$, which is an oil having a pungent taste, but no odour in the cold. The *picrate*,

$$C_{11}H_{13}NO,C_6H_3N_3O_7,$$

crystallises well, and melts at 139—140°, whilst the *platinochloride* forms an orange-yellow, crystalline powder.

β-Bromethylcinnamylamide, $C_2H_4Br{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh$, obtained from cinnamic chloride and β-bromethylamine hydrobromide, crystallises from light petroleum in white plates melting at 90—91°. Alcoholic potash converts it into *μ-cinnamenyloxazoline*,

$$\begin{matrix}CH_2{\cdot}O\\|\\CH_2{\cdot}N\end{matrix}>C{\cdot}CH{:}CHPh,$$

which crystallises from light petroleum in transparent prisms containing light petroleum; this is evolved on exposure to the air or over sulphuric acid, and the substance then melts at 52—53°, becoming plastic at 48°. The *picrate*, $C_{11}H_{11}NO,C_6H_3N_3O_7$, forms yellow needles melting at 188—189°, and the *platinochloride*,

$$(C_{11}H_{11}NO)_2,H_2PtCl_6,$$

an orange-yellow, crystalline powder melting with decomposition at 193—194°.

β-Bromopropylcinnamylamide, $CHMeBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh$, crystallises from benzene or light petroleum in white plates melting at 79—80°. The *β-methyl-μ-cinnamenyloxazoline*,

$$\begin{matrix}CHMe{\cdot}O\\|\\CH_2{-}N\end{matrix}>C{\cdot}CH{:}CHPh,$$

obtained from it, separates from light petroleum in crystals containing light petroleum, which is given off on exposure to the air, the compound then melting at 80—81°. The *picrate*, $C_{12}H_{13}NO,C_6H_3N_3O_7$, crystallises in delicate needles, and melts at 182—183°, and the *platinochloride*, $(C_{12}H_{13}NO)_2,H_2PtCl_6$, melts with frothing at 197—198°.

γ-Bromopropylcinnamylamide, $CH_2Br{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh$, forms hexagonal plates, melts at 74°, and is converted by alkalis into *μ-cinnamenylpentoxazoline*, $CH_2<\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}N\end{matrix}>C{\cdot}CH{:}CHPh$, which also contains light petroleum and melts, after removal of the latter, at 55—56°. The *picrate*, $C_{12}H_{13}NO,C_6H_3N_3O_7$, melts at 196°, and the *platinochloride*, $(C_{12}H_{13}NO)_2,H_2PtCl_6$, at 192—193° with decomposition.

H. G. C.

Thiazole Compounds. By P. Spica and G. Carrara (*Gazzetta*, **21**, 421—432).—The authors have prepared the following compounds by Wöhler's method :—

Unsymmetrical dimethylthiocarbamide, $NH_2{\cdot}CS{\cdot}NMe_2$, is obtained in colourless, hard, deliquescent crystals melting at 81—82°, and is very soluble in water and absolute alcohol.

Unsymmetrical diethylthiocarbamide, $NH_2{\cdot}CS{\cdot}NEt_2$, is a colourless, deliquescent substance, which crystallises with difficulty, is soluble in water and absolute alcohol, and melts at 169—170°.

Unsymmetrical diisoamylthiocarbamide, $NH_2{\cdot}CS{\cdot}N(C_5H_{11})_2$, is obtained in colourless scales, moderately soluble in water, easily soluble in absolute alcohol, and melts at 208—209°. It is very like camphor in appearance and in its behaviour when floating on water.

Unsymmetrical diisoamylselenocarbamide, $NH_2{\cdot}CSe{\cdot}N(C_5H_{11})_2$, is obtained by the action of potassium selenocyanate on diisoamylamine in colourless scales melting without decomposition at 171—172°. By exposure to light or by heating, it turns first red and then green. It crystallises with 2 mols. H_2O, which it retains in a vacuum over sulphuric acid, but loses on heating at 100° in a current of air.

On condensation with halogen derivatives of ketones, the unsymmetrical bi-substituted thiocarbamides should behave analogously to the symmetrical derivatives, and yield thiazole derivatives of the constitution $\begin{matrix} S{\cdot}NR'_2 \\ | \\ CH{:}CR \end{matrix}\!\!>\!N$.

The authors endeavoured unsuccessfully to prepare these compounds by the use of chloracetone and bromacetophenone in the following cases:—

A mixture of unsymmetrical dimethylthiocarbamide with chloracetone in molecular proportion was heated on a water-bath until no further odour of chloracetone was observed. The residue was taken up with water, made alkaline with caustic soda, and the solution extracted with ether. The ethereal extract contains dimethylamine and an unknown base, the platinochloride of which contains 40·02 per cent. of platinum; the mother liquor, after complete extraction with ether, yields a yellowish precipitate when acidified with hydrochloric acid. This is partly soluble in alcohol and chloroform, sparingly in light petroleum, and sparingly and partially soluble in water; it contains sulphur but no chlorine, melts partially at about 90°, and decomposes above 100°; it is probably impure α-methylhydroxythiazole, but the quantity obtained was too small for purification and analysis.

The solution in absolute alcohol of equivalent quantities of unsymmetrical dimethylthiocarbamide and bromacetophenone is evaporated to dryness on the water-bath, the residue dissolved in absolute alcohol, and fractionally crystallised. On recrystallisation from dilute alcohol, long needles melting at 71—72°, and agreeing in properties with rhodanacetophenone, first separate; the mother liquor contains a deliquescent substance agreeing in properties with dimethylamine hydrobromide. When unsymmetrical diisoamylthiocarbamide and bromacetophenone are treated in the same manner, the substance melting at 71—72°, and a white, crystalline product, which seems to be diisoamylamine hydrobromide, are obtained. When the alcoholic solution of dibenzilethiocarbamide and chloracetone is treated in the manner indicated above, a product is obtained which, on solution in

alcohol and precipitation with light petroleum, yields dibenzylamine hydrochloride; the mother liquors contain a yellow substance, soluble in water and caustic alkalis, sparingly soluble in ether, insoluble in acids or ammonium carbonate solution, and melting at 96°. No analyses were made, but the substance is supposed to be methylhydroxythiazole. Similar results are obtained on heating unsymmetrical dibenzilethiocarbamide with chloracetone on the water-bath without any solvent, treating with caustic soda, and extracting with ether, as before indicated. Symmetrical diphenylthiocarbamide and chloracetone, treated in the same manner, yield the base melting at 138°, prepared by Taumann. Unsymmetrical dibenzilethiocarbamide and bromacetophenone, when heated together, give benzilamine hydrobromide and the substance melting at 71—72°. To show that this compound is really rhodanacetophenone, it was converted into carbaminethioacetophenone by boiling for a short time with strong hydrochloric acid; on prolonged ebullition, α-phenyl-μ-hydroxythiazole was obtained.

The general reaction between unsymmetrical bi-substituted thiocarbamides and halogen derivatives of ketones, is best represented by the following equation:—

$$R{\cdot}CO{\cdot}CH_2Cl + S{:}C(NH_2){\cdot}NR'_2 = N{:}C{\cdot}S{\cdot}CH_2{\cdot}R{\cdot}CO + NHR'_2{\cdot}HCl.$$

W. J. P.

Quinazolines. By S. Gabriel and R. Jansen (*Ber.*, **24**, 3091—3098; compare Abstr., 1890, 1442).—Orthamidobenzylacetamide, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}COMe$ [1 : 2], when distilled, yields a substance which must be β-methyldihydroquinazoline, $C_6H_4{<}\begin{matrix}CH_2{\cdot}NH\\ |\\ N{=}CMe\end{matrix}$, for when methylated it yields the same $\beta\gamma$-dimethyldihydroquinazoline, $C_6H_4{<}\begin{matrix}CH_2{\cdot}NMe\\ |\\ N{=}CMe\end{matrix}$, which is obtained by distilling orthamidobenzylacetomethylamide, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe{\cdot}COMe$. Hence, by analogy, the substance formed when orthonitrobenzylformamide,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}COH,$$

is reduced with zinc and hydrochloric acid must be dihydroquinazoline, $C_6H_4{<}\begin{matrix}CH_2{\cdot}NH\\ |\\ N{=}CH\end{matrix}{\cdot}$

Orthonitrobenzylamine is best prepared by mixing orthonitrobenzyl chloride (24·5 grams) with potassium phthalimide (25·5 grams) in benzyl cyanide (35 c.c.), heating the whole on a water-bath until all the water is expelled, and finally keeping it for half an hour at 180°. The cyanide is then driven over with steam, and the residue purified by boiling with a little alcohol. Nitrobenzylphthalimide (31 grams = 75 per cent. of the theoretical yield) is left behind; it yields orthonitrobenzylamine when heated (15 grams) with hydrochloric acid of sp. gr. 1·19 (60 c.c.) for three hours at 185—190°. The hydrochloride is obtained by separating the phthalic acid and concentrating the filtrate. The *picrate*, $C_7H_8N_2O_2,C_6H_3N_3O_7$, forms sparingly soluble, yellow needles, and melts at 206—208°. *Ortho-*

nitrobenzylcarbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, is obtained in needles melting at 150°, by concentrating an aqueous solution of potassium cyanate and orthonitrobenzylamine hydrochloride.

When orthonitrobenzyl chloride (10 grams) is allowed to remain in a closed flask with 10 per cent. alcoholic ammonia (100 c.c.) for 10 days at the ordinary temperature, crystals of *diorthonitrobenzylamine*, $NH(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$ (5·5 grams), are deposited. These can be crystallised from hot alcohol; they melt at 99—100°. The *hydrochloride*, $C_{14}H_{13}N_3O_4{\cdot}HCl$, melts above 220°, becoming charred. The *platinochloride*, $(C_{14}H_{13}N_3O_4)_2,H_2PtCl_6$, forms small, yellow needles, very sparingly soluble in water. The *nitrosamine*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2N{\cdot}NO$, is obtained in lustrous needles melting at 120°, when nitrous acid is added to an acetic acid solution of the base. The mother liquor from the diamine, on concentration, leaves a residue (4 grams), from which nitrobenzylamine hydrochloride (2 grams) can be obtained by extracting with alcohol a concentrated, filtered, aqueous solution of the residue.

When orthonitrobenzyl chloride (15 grams) is dissolved in alcohol (150 c.c.) and warmed for one hour in a stoppered flask in the water-bath with 33 per cent. aqueous methylamine (45 c.c.), and the residue left after evaporation of the alcohol is treated with water, it yields *diorthonitrobenzylmethylamine*, $NMe(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, as an insoluble oil, which crystallises after a time; when recrystallised from methyl alcohol, it forms yellowish prisms melting at 62—64°. The aqueous solution is concentrated to a small bulk, treated with 33 per cent. aqueous potash, and extracted with ether. The brownish oil obtained on evaporating the ether is mixed with hydrochloric acid, and the solution evaporated. The *orthonitrobenzylmethylamine hydrochloride*, $NO_2{\cdot}C_6H_4{\cdot}NHMe,HCl$ (9·5 grams), thus obtained, crystallises from 95 per cent. alcohol in tables, and melts at 175—176·5°. When this salt (6 grams) is boiled for a quarter of an hour in a reflux apparatus with dry sodium acetate (3 grams) and acetic anhydride (12 c.c.), the mixture concentrated and treated with water, *orthonitrobenzylacetomethylamide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe{\cdot}COMe$, separates as an oil, which finally crystallises; from light petroleum, it can be obtained in small, lustrous, white crystals melting at 57—58°. This substance, finely powdered (1 gram), is mixed with water (15 c.c.) and concentrated hydrochloric acid, and treated with zinc. After remaining for a time, the clear solution is poured off, and treated with excess of aqueous soda; the *orthamidobenzylacetomethylamide*,

$$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe{\cdot}COMe,$$

is extracted with ether, and recrystallised from this solvent; it forms a fine powder melting at 94—95°. This was heated gently in a small distillation-flask until no more water was expelled, *βγ-dimethyldihydroquinazoline*, $C_6H_4<\begin{matrix}CH_2{\cdot}NMe\\ |\\ N=CMe\end{matrix}$, then distils over at 300—305° as a pale-yellow oil which solidifies on cooling. It crystallises from ether in small, white needles, softens at 70°, and melts at 75—77°. Its solution in water is alkaline, and has a bitter taste. It dissolves also in hydrochloric acid, and the solution forms double salts with platinum

chloride, potassium dichromate, and picric acid. The *picrate* softens at 210°, and melts at 215—217°.

β-Methyldihydroquinazoline unites with methyl iodide, forming colourless crystals of the methiodide. When these are dissolved in water, and the solution treated with potash, a yellow oil separates, which has all the properties of βγ-dimethylhydroquinazoline, described above.

Dihydroquinazoline, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ |\\ N=CH\end{matrix}$, has now been obtained crystalline. From benzene it separates in small, yellowish crystals which soften at 115°, and melt at 127°. The *hydrochloride*, $C_8H_8N_2,HCl$, crystallises from alcohol. C. F. B.

Choline. By E. Schmidt (*Arch. Pharm.*, **229**, 467—486).—Choline platinochloride melts at 232—233° when heated in a narrow capillary tube, but generally at 240—241° with much frothing; Bode gives 233—234° (*Inaug. Diss., Marburg*, 1889), and Jahns gives 225° (Abstr., 1891, 94).

Gram (*Arch. exp. Path. Pharm.*, **20**, 116) says that neurine and choline platinochlorides are so similar in crystalline form as to be distinguishable only by their difference in colour. The author finds that choline platinochloride forms large, soluble, red, tabular, monoclinic crystals, arranged like steps; whilst neurine platinochloride crystallises in small, individual, sparingly soluble, orange-red, regular octahedra, and melts at 211—213°.

To convert choline into neurine, it is heated with fuming hydriodic acid at 140°, and the product is treated with moist silver oxide. To convert neurine into choline, it is heated with hydriodic acid, and the product then heated with silver nitrate in aqueous solution (compare Bode, *loc. cit.*).

Choline platinochloride is not converted into neurine platinochloride when heated with hydrochloric acid in the water-bath, as stated by Gram (*loc. cit.*).

Choline lactate is not converted into neurine lactate when heated in water, as stated by Gram, but a *lactocholine platinochloride*, $NMe_3Cl\cdot CH_2\cdot CH_2\cdot O\cdot CHMe\cdot COO\cdot CH_2\cdot CH_2\cdot NMe_3Cl,PtCl_4,2H_2O$, is obtained if, after the action has continued for six days, neutral platinic chloride is added in considerable quantity, and the mixture rapidly evaporated. This salt forms columnar crystals with bevelled ends, melts with decomposition at 220°, and dissolves easily in water, but more sparingly in alcohol.

An aqueous solution of choline does not contain any neurine after it has been kept for four months, whether the solution be concentrated or dilute. In two experiments with hay infusion, the author found that, under the influence of the organisms contained therein, choline is converted, to a small extent, into neurine; further experiments gave somewhat uncertain results. A. G. B.

Adenine. By M. Krüger (*Zeit. physiol. Chem.*, **16**, 160—172).—The knowledge of the nucleïn bases, derived from nucleïc acid, is of

importance, as the origin of uric acid in the system may probably be arrived at by their study, especially if adenine and hypoxanthine can be shown to belong to the uric acid group, which includes xanthine and guanine. Adenine was prepared from tea-extract, and estimated by the help of sodium picrate (Bruhns, Abstr., 1890, 534). It can be prepared free from water of crystallisation by adding excess of ammonia to concentrated solutions of its hydrochloride; four-sided pyramids are thus obtained. A 0·5 per cent. aqueous solution gives no precipitate with potassium ferrocyanide or ferricyanide until acetic acid is added, when thin, crystalline plates are obtained. Ferric chloride gives a red coloration unaltered by heat. Copper sulphate produces a greyish-blue, amorphous precipitate, containing 2 atoms of copper to 1 mol. of SO_3; it is, therefore, a mixture of copper-adenine and adenine-copper sulphate. With chromic acid, it forms a dichromate,

$$(C_5H_5N_5)_2,H_2Cr_2O_7;$$

this crystallises as six-sided plates. With chloracetic acid, it forms prismatic crystals of a chloracetate, $C_5N_5N_5,2CH_3ClO_2$. With hydrochloric acid at 135°, it is completely decomposed (Kossel), and it appeared of importance to determine the products formed. On carrying out the reaction in sealed tubes, it was found that the products were carbonic anhydride, carbonic oxide, and ammonium chloride. Four atoms of its nitrogen appear in the form of ammonia; consequently no methylamine group is present in adenine. Glycocine is also formed, and the following equation represents what occurs:—$C_5H_5N_5 + 8H_2O = 4NH_3 + CO_2 + 2CH_2O_2 + C_2H_5NO_2$. No formic acid is, however, found as such; the strong acid, the pressure, and the temperature break it up completely into carbonic oxide and water. Similarly treated, hypoxanthine undergoes the following reaction:—$C_5H_4N_4O + 7H_2O = 3NH_3 + CO_2 + 2CH_2O_2 + C_2H_5NO_2$. Comparing these results with those obtained by Schmidt (*Annalen*, **217**, 311) in relation to xanthine ($C_5H_4N_4O_2 + 6H_2O = 2CO_2 + CH_2O_2 + 3NH_3 + C_2H_5NO_2$), it is seen that xanthine and hypoxanthine yield qualitatively the same products; the quantitative difference is that the relation of $CO_2 : CH_3O_2$ is 1 : 2 in hypoxanthine, and 2 : 1 in xanthine. Uric acid, under the influence of concentrated hydriodic acid at 160—170°, also yields glycocine, carbonic anhydride, and ammonia (Strecker, *ibid.*, **146**, 142). W. D. H.

Adenine and Hypoxanthine. By G. Bruhns and A. Kossel (*Zeit. physiol. Chem.*, **16**, 1—12).—By Beckmann's method (*Zeit. physikal. Chem.*, **4**, 532) the molecular weight of adenine was found to be sufficiently near 135 to warrant the author's previous assumption that its formula is $C_5H_5N_5$.

On oxidation, uric acid, xanthine, and their derivatives yield products which show they contain an alloxan nucleus. Whether hypoxanthine and adenine contain this is uncertain, but by bringing acid groups into their molecule, it was hoped to obtain an answer to this question. For this purpose, the action of ethyl chlorocarbonate on hypoxanthine was investigated; 4 grams of hypoxanthine hydrochloride were mixed with 3 grams of sodium hydroxide and 5 grams of ethyl

chlorocarbonate, and after 24 hours, the precipitate which formed was collected, and was recrystallised from hot water, when tables about 7 mm. by 1 mm. were obtained, melting at 185—190°. They were sparingly soluble in alcohol, ether, and cold water, but readily in hot water, sodium hydroxide, and hydrochloric acid. Their composition was found to be $C_5H_3N_4O{\cdot}COOEt$, that is, the substance is the urethane of hypoxanthine. It was, however, found unsuitable for experiments on oxidation, and attention was then directed to the bromine derivatives of adenine. The action of bromine appears to take place in the following stages:—

(1.) $C_5H_5N_5 + Br_2 = C_5H_4N_5Br + HBr.$
(2.) $C_5H_4N_5Br + HBr = C_5H_4N_5Br,HBr.$
(3.) $C_5H_4BrN_5,HBr + 2Br_2 = C_5H_4BrN_5,Br_4,HBr.$

The final product, which is red, is *bromadenine tetrabromide hydrobromide.*

Bromadenine, $C_5H_4BrN_5$, crystallises in thin plates: it is sparingly soluble in water, but very readily in ammonia and fixed alkalis, and fairly soluble in mineral acids, with which it forms salts. The sulphate, $(C_5H_4BrN_5)_2,H_2SO_4 + 6H_2O$, hydrochloride, $C_5H_4BrN_5,HCl$, and nitrate, $C_5H_4BrN_5,HNO_3$, were prepared. The picrate,

$$C_5H_4BrN_5,C_6H_2(NO_2)_3{\cdot}OH + H_2O,$$

is very similar in its properties to adenine picrate. Bromadenine, like adenine, also gives metallic derivatives with silver nitrate, mercuric chloride, cadmium chloride, &c.

Attempts to obtain an oxyadenine or ethoxyadenine by the method adopted by Fischer in regard to caffeïne (*Ber.*, **14**, 637; **15**, 29, 453; *Annalen*, **215**, 253) failed. Difficulties were also found in an attempt to prepare chloradenine, but at last it was obtained by heating adenine with phosphorus pentachloride in a sealed tube at 160—170° for several hours. W. D. H.

Behaviour of Cupreïne and Quinine with Methyl Iodide. By O. Hesse (*Annalen*, **266**, 240—245).—When quinine is boiled with excess of methyl iodide in methyl alcoholic solution, it yields the methiodide, $C_{20}H_{24}N_2O_2,MeI + H_2O$, as sole product; if, however, the reaction is carried out at 80—100°, the dimethiodide, $C_{20}H_{24}N_2O_2,2MeI, + 3H_2O$ is formed. The *dimethochloride*, prepared from the methiodide, crystallises in pale-yellow needles, and is readily soluble in water. The *platinochloride*, $C_{20}H_{24}N_2O_2,Me_2PtCl_6 + 2H_2O$, is a dark-yellow, crystalline compound, sparingly soluble in cold water. The *aurochloride*, $C_{20}H_{24}N_2O_2,2MeAuCl_4$, is a yellow, flocculent substance, and decomposes at about 100°.

When a methyl alcoholic solution of cupreïne is boiled with excess of methyl iodide, the methiodide is formed, but if the mixture is heated at 80—100°, *cupreïne dimethiodide*, $C_{19}H_{22}N_2O_2,2MeI + 3H_2O$, is produced. This compound crystallises in prisms, melts at about 210° with decomposition, and is moderately easily soluble in hot water. The corresponding *methochloride* crystallises in pale-yellow needles, and is moderately easily soluble in water and alcohol; its *platino-*

chloride, $C_{19}H_{22}N_2O_2,Me_2PtCl_6$, is an orange, granular compound, very sparingly soluble in cold water.

When cupreïne is heated with methyl iodide and sodium methoxide in methyl alcoholic solution, it is converted into a mixture of the mono- and di-methiodides of quinine, as stated by Grimaux and Arnaud (Abstr., 1891, 1121). F. S. K.

Preparation of Homologues of Quinine. By E. Lippmann (*Monatsh.*, **12**, 512—514).—The yield of methylquinine obtained by Claus and Mahlmann's process (*Ber.*, **14**) is unsatisfactory, owing to a large quantity of the quinine methiodide escaping decomposition; the author finds that the following method gives much better results. The quinine methiodide is boiled with excess of silver oxide, the silver iodide filtered off, and the solution treated with a slight excess of dilute sulphuric acid, whereby the sparingly soluble sulphate is precipitated in the form of needles. The crystalline mass is dried on a porous plate, and heated in sealed tubes at 140° with excess of sodium hydroxide solution. Under these conditions, the quinine methohydroxide, $C_{20}H_{24}N_2O_2,MeOH$, loses water, and is converted into methylquinine, $C_{20}H_{23}MeN_2O_2$, which can be separated from the product by shaking with ether. G. T. M.

Isocinchonine. By O. Hesse (*Annalen*, **266**, 245—248).—This article is principally controversial; the author also describes experiments which point to the conclusion that commercial cinchonine sulphate may sometimes contain two isomeric alkaloïds, one of which yields isocinchonine, the other cinchoniline. F. S. K.

Isocinchonines. By E. Jungfleisch and E. Leger (*Compt. rend.*, **113**, 651—654; compare Abstr., 1891, 1121).—A continuation of the discussion with Hesse. They find that the isocinchonine of Comstock and Koenig is identical with cinchoniline. C. H. B.

Digitaleïne. By J. Houdas (*Compt. rend.*, **113**, 648—651).—The author has shown that the soluble digitalines of Schmiedeberg consist almost entirely of one glucoside, to which he gives Nativelle's name *digitaleïne*. It is characterised by the following properties:—When amyl alcohol is added to an aqueous solution of digitaleïne, the latter is rapidly precipitated in a crystalline form. If a hot mixture of amyl and ethyl alcohols is used, the solution, on cooling, deposits long, nacreous lamellæ, which contain amyl alcohol and water of crystallisation. If these crystals are dissolved in boiling water, the amyl alcohol expelled by prolonged ebullition, and the liquid mixed with its own volume of ethyl alcohol of 95°, long needles separate in stellate groups on cooling. The crystals contain ethyl alcohol and water, and are more soluble than those containing amyl alcohol. Similar results are obtained with methyl alcohol. It follows that when an alcohol of the ethyl series is added to a solution of digitaleïne, a crystalline compound of the alcohol and hydrated digitaleïne is obtained, and its solubility in water is greater the lower the molecular weight of the alcohol. Phenols seem to behave in a

similar manner, and ordinary phenol gives a well-crystallised compound which will be described subsequently. The crystals lose their alcohol and water at 110°. They dissolve somewhat slowly in cold water, but very rapidly in boiling water. Digitaleïne, however, has not yet been crystallised from aqueous solutions. When the liquid evaporates, the glucoside is left as a vitreous residue.

Digitaleïne is very slightly soluble in alcohol, and is practically insoluble in chloroform, ether, and light petroleum. In aqueous solution, it has a lævorotatory power; $[\alpha]_D = -49{\cdot}25°$. When heated, it shows no distinct melting point, but agglomerates at about 250°, intumesces at about 270°, and is completely caramelised at 280°. It seems to be unaffected by exposure to air, and its aqueous solution can be kept for a long time without undergoing any change. It is precipitated by tannin or ammoniacal lead acetate, and dissolves in cold hydrochloric acid without coloration; but if the solution is heated, it becomes violet-red, with a slight, greenish fluorescence. Sulphuric acid, diluted with its own volume of water, produces a yellowish coloration in the cold, changing to red, and finally to black, on heating.

The elementary composition is represented by the formula $C_{62}H_{52}O_{34}$, and agrees with that given by Schmiedeberg. When treated with very dilute sulphuric acid, digitaleïne yields two crystallisable glucosides without any glucose. C. H. B.

Hydrastine. By M. Freund and C. Dormeyer (*Ber.*, **24**, 3164).—The question as to whether the bromomethylhydrohydrastinine, $C_{12}H_{14}NO_2Br$, described by the authors (Abstr., 1891, 1518), is related to the compound obtained by Merlin (Abstr., 1884, 1385; 1887, 164) from dimethylpiperidine and bromine, and is, therefore, an ammonium bromide, has yet to be settled. A. R. L.

Lupanine: the Alkaloïd of the Blue Lupine. By C. Siebert (*Arch. Pharm.*, **229**, 531—546).—Hagen (Abstr., 1886, 163) ascribes the formula $C_{15}H_{25}N_2O$ to lupanine; this formula is contrary to the law of even atomicities, and should be doubled, except that Hagen's results do not exclude the formula $C_{15}H_{24}N_2O$.

The crushed seeds were extracted eight times with two successive quantities of alcohol containing hydrochloric acid; the extract was distilled, the residue made alkaline with potassium hydroxide, and extracted with ether; the ethereal solution was shaken with dilute hydrochloric acid, and the aqueous solution of the hydrochloride thus obtained was again treated with potassium hydroxide and ether to separate the pure base. The seeds yielded 0·33 per cent. of lupanine; Hagen obtained 0·19—0·22 per cent.

Lupanine is freely soluble in cold water to a clear solution, and also in cold alcohol (compare Hagen, *loc. cit.*). The hydrochloride, $C_{15}H_{24}N_2O,HCl + 2H_2O$, forms long, white, needle-shaped crystals, easily soluble in water, alcohol, and chloroform, but not in ether; when dried at 90°, it melts at 127°. The hydriodide, $C_{15}H_{24}N_2O,HI + 2H_2O$, forms yellowish crystals, and, when dried at 100°, melts at 184—185°. The *hydrobromide*, $C_{15}H_{24}N_2O,HBr + 2H_2O$, forms large, white,

tabular crystals, melts at 111°, and is soluble in water and alcohol. The platinochloride forms nodular crystals with 4 mols. H_2O. The aurochloride separates on addition of water to its alcoholic solution in long, prismatic crystals; it is anhydrous, dissolves in alcohol and water, and melts at 198—199°. The methiodide melts at 248—249° (Hagen gives 215°).

Lupanine is not changed by heating with fuming hydrochloric acid at 200°, or with concentrated aqueous or alcoholic sodium hydroxide solution at the ordinary pressure. When heated with soda-lime, the lupanine molecule is split up, 1 atom of nitrogen appearing as ammonia, and the other as a pyridine base; an unsaturated hydrocarbon is also obtained, and may be taken as evidence of a side chain in the molecule.

By oxidation with potassium permanganate in acid solution, lupanine yielded carbonic anhydride, a little ammonia, a neutral substance, $C_{15}H_{20}N_2O_3$, and a nitrogenous acid. A. G. B.

Nucleïns. By H. Malfatti (*Zeit. physiol. Chem.*, **16**, 68—86).—Nucleïns may be divided into two groups: the true nucleïns from cell-nuclei, which yield xanthine bases on decomposition, and the paranucleïns from egg yolk and milk, which do not. The question arises whether the artificial nucleïn of Liebermann, prepared by the addition of metaphosphoric acid to albumin, belongs to the first or second group. The preparation of nucleïc acid from nucleïn by Altmann (*Du Bois Reymond's Archiv, physiol. Abth.*, 1889, 514) gives a further means of distinguishing between the two groups. An artificial nucleïn, containing 6·1 per cent. of phosphorus, was prepared from serum-albumin; after dissolving in ammonia and reprecipitating by acetic acid several times, the percentage of phosphorus sank to 1·6. This is due to the separation of a nucleïc acid rich in phosphorus. This is soluble in ammonia; from this solution it is not precipitable by acetic acid, but it is by hydrochloric acid; it yields no trace of xanthine derivatives, and therefore belongs to the class of paranucleïc acids, and the nucleïn from which it originates to the class of paranucleïns. The opinion, however, is advanced that the nucleïns and paranucleïns are not so distinct as might be supposed, but that the true nucleïns are either simple additive or substitution compounds of paranucleïns and the xanthine bases in question.

After incineration and heating with potassium nitrate, phosphorus estimations were made, by titration with uranium acetate.

W. D. H.

New Proteïd from Human Blood Serum. By C. Chabrié (*Compt. rend.*, **113**, 557—559).—Serum, neutralised by acetic acid, is coagulated and evaporated at 100°. The mass is extracted by distilled water at 100°, the water being half the original bulk of the serum. The filtered liquid is somewhat cloudy; the addition of 89° alcohol gives a white, flocculent precipitate collecting together after some hours. The precipitate collected and dried in the air is soluble in water, from which it is reprecipitated by alcohol. It contains an organic substance resembling albumin, and yields 0·637 per cent. of ash consisting of phosphates, and not containing calcium or

chlorides. It is proved to be a new substance by the following reactions:—It is coagulated by alcohol, but not by heat, even in presence of acetic acid. Nitric acid gives a precipitate soluble in slight excess. Potassium ferrocyanide in presence of acetic acid gives a milkiness, increasing with time. Phosphotungstic acid yields a precipitate; ammonium phosphomolybdate gives a white precipitate on heating. Acid mercury nitrate gives a yellow precipitate; Millon's reagent a white one, becoming rose-coloured on heating. The substance yields no sublimate and no biuret reaction. No result follows the addition of a saturated solution of magnesium sulphate; sodium sulphate causes a white precipitate.

On account of its analogies with albumin, it is proposed to name the new substance *albumone*. It was found to the extent of 1/12,000 by weight in the blood of a healthy man. In that taken from a patient suffering from nephritis, it formed 0·087 per cent.

Albumone is strongly lævorotatory, but the opalescence of its solution prevents the determination of the amount of rotation with accuracy. It does not dialyse.

It differs from Béchamp's néphrozymase obtained from urine, this substance saccharifying starch at 60°, whereas albumone exerts no such action. W. T.

Physiological Chemistry.

Influence of Nutrition on the Composition of the Blood-ash. By K. Landsteiner (*Zeit. physiol. Chem.*, **16**, 13—19).—Verdeil states (*Annalen*, **69**, 89) that the salts of the blood vary with those of the food; an animal fed on flesh has in the blood alkaline phosphates, which are replaced by carbonates when a vegetable diet is given. Against this view we have the fact (Jarisch, *Wiener med. Jahrb.*, 1871, 435; 1877, 1) that the ash of the blood of different animals (men, dogs, horses, oxen) is practically the same, although their diet is different. In the present research, 15 young rabbits were dieted for three months and a half on hay, and another 15 on milk. The ash in the blood was in both cases practically the same, qualitatively and quantitatively; such differences as were noticed being explicable by differences in the relation of corpuscles to plasma. In animals with equal amounts of hæmoglobin in their blood, the corpuscular element was probably identical, and here, whatever the diet, the $Na_2O : K_2O$ quotient and the other analytical details obtained were also identical. W. D. H.

Bile during Inanition. By S. M. Lukjanow (*Zeit. physiol. Chem.*, **16**, 87—142).—The experiments were carried out on guinea pigs, and may be divided into five groups; the first group consisted of normal animals; the remaining four groups of animals in different stages of

inanition. Very complete analytical tables relating to each experiment are given.

The animals were found to lose on the average 1 per cent. of body weight in four hours four minutes. At the commencement of inanition, the relative weight of the liver is the smallest; in the middle period it rises, returning to the normal, and it continues to rise to the end. In the initial and middle stages, the liver is poor in water; in the final stage, the amount of water rises, first to the normal, and then above it. In the blood there is a progressive loss of water.

In the first stage (loss of body weight 5·53 per cent.), the amount of bile per hour per 10 grams of liver substance, and per 1 kilo. of body weight is rather greater than the normal; it then progressively sinks, but most rapidly in the middle periods (loss of body weight, 16 to 25 per cent.). This is represented in charts by means of curves. At first the bile is dilute, but, later, becomes more concentrated, soon, however, reaching a maximum at which it remains; this increased percentage of solids is chiefly due to the bile salts. The lessening found in the amount of bile secreted is not solely due to concentration, but also to a diminution in the solids secreted. The energy of secretion of bile during inanition is thus less than in normal animals; but the diminution in energy is most marked during the first half of the hunger period. W. D. H.

Carbohydrates of Putrefying Human Urine. By G. Treupel (*Zeit. physiol. Chem.*, **16**, 47—67).—The formation of fatty acids in normal urine when putrefaction sets in is due to the decomposition of its carbohydrates (dextrose and animal gum). In the present research, the furfuraldehyde and α-naphthol reaction was employed for the estimation of sugar (see Abstr., 1891, 1559), the results being controlled, in some cases, by Baumann's benzoic chloride method. It was found, that as putrefaction advanced the carbohydrate in the urine diminished, but a small quantity always remained, even after very prolonged periods (30 to 47 days). If the urine was exposed to the air, putrefaction and the diminution of carbohydrate occurred more rapidly than in closed vessels. Increase of the temperature to 35° also hastened the process. W. D. H.

Ethereal Hydrogen Sulphates in the Urine, and Disinfection of the Alimentary Canal. By A. Rovighi (*Zeit. physiol. Chem.*, **16**, 20—46).—From experiments on the author's person, on various patients, and on dogs, the following conclusions are drawn:—

1. The quantitative estimation of the ethereal hydrogen sulphates in the urine is a trustworthy criterion of the amount of putrefactive change in the intestine.

2. The amount of these substances passed varies with the time of day, so that it is necessary to examine a specimen of the mixed 24 hours' voidings.

3. In children, the amount passed is less than in adults.

4. Oil of turpentine and camphor in large doses lessen the putrefac-

tion in the dog's intestine, and, consequently, the output of ethereal sulphates in the urine.

5. In the human being, given either by mouth or rectum, these drugs have not the same efficacy.

6. Tannin clysters lessened, but only very slightly, the ethereal hydrogen sulphate of the urine in a case of enteroperitonitis, where their amount was excessive.

7. A saturated solution of boric acid injected into the intestine is more effective; but the absorption of the acid by the intestinal mucous membrane is dangerous.

8. The use of Carlsbad salts and Marienbad water is followed by an increased output of ethereal hydrogen sulphates for the first few days; this is followed by a very marked diminution.

9. Kephir ($1\frac{1}{2}$ litres per diem) is an excellent means of lessening intestinal putrefaction. Its action depends, in part at least, on the lactic acid it contains. W. D. H.

Physiological Action of Strontium Salts. By J. V. Laborde (*Compt. rend. Soc. Biol.*, 1890, 708—716; 1891, 562—566; compare Abstr., 1891, 99).—The action of the sulphate, normal tartrate, and orthophosphate of strontium was compared experimentally with that of the corresponding salts of potassium. The results again showed the innocuity of the strontium compounds; the lactate and tartrate have a slight diuretic action. Elimination takes place chiefly through the fæces. It is partly assimilated, being found in the liver and bones, and, to a small extent, is eliminated in the urine.

Further experiments with the bromide were confirmatory of the foregoing. W. D. H.

Physiological Action of Camphors, and of their Compounds with Chloral. By Schmitt (*Compt. rend. Soc. Biol.*, 1890, 678—683).—In a warm-blooded animal, camphor causes excitation of the central nervous system leading to general convulsions, an increase in the depth of respiration, a slowing of the heart, with increased force of its beats, and a marked elevation of blood pressure. Borneol and menthol, on the other hand, produce a sedative action on the nerve centres, borneol being the more powerful. Borneol, however, diminishes the frequency and depth of respiration, the number and force of the heart beats, and produces a fall of blood pressure; whilst menthol increases respiratory and cardiac activity, leading to a heightened intravascular pressure.

In experiments on rabbits, it was found that by giving borneol after chloral hydrate, the depressing action of the chloral was augmented by that of the borneol, whereas menthol in part counteracted this depression. Starting from this, the physiological action of compounds of chloral with the camphors was investigated.

Camphor dissolves in anhydrous chloral, but does not form definite compounds with it, whereas borneol and menthol do. The mixture of camphor and chloral produces the same effects as if the drugs were given successively, the convulsive effects of the camphor being masked by the sedative action of the chloral.

Chloral bornylate, $CCl_3 \cdot CH(OH) \cdot OC_{10}H_{17}$, forms white crystals insoluble in water, and melts at 45—55°. It is very toxic, producing a lowering of blood pressure and temperature to a greater extent than can be accounted for by the amount of chloral it contains.

Chloral menthylate, $CCl_3 \cdot CH(OH) \cdot OC_{10}H_{19}$, is a transparent, yellowish liquid, of the consistence of glycerol, insoluble in water, soluble in alcohol of 90°, and in oil. When distilled with water, it dissociates into menthol and chloral hydrate; an analogous dissociation in the body probably accounts for its physiological action. It irritates the mucous membranes when applied locally. Given subcutaneously or by the mouth, it leads to paralysis of the posterior limbs, and then to sleep; the soporific action is the same in its strength and duration as that produced by a corresponding dose of chloral hydrate, although its onset is somewhat delayed. The paralytic effects and lessening of reflex action are due to the menthol. The movements of respiration and of the heart are effected in the same way as with chloral; the depression of temperature is, however, not so marked. Blood pressure is first lowered, then rises, remaining stationary at a lower level than the original. Thus, to some extent, the menthol corrects the depression due to the chloral. W. D. H.

Toxic Action of Blood and of Various Tissues. By J. Héricourt and C. Richet (*Compt. rend. Soc. Biol.*, 1890, 695—696).—The blood of one animal is poisonous to that of another species; thus the toxic dose of dogs' blood, as tested in the rabbit, is 40—45 grams per kilo. of body weight. Birds' blood is more poisonous, its toxic dose being 7 grams. Mosso has previously shown, particularly with fishes' blood, that the poisonous effects of the serum are due to its proteïds (ichthyotoxin); and the present experiments confirm this conclusion, as the alcoholic extracts of the blood and spleen, which are, of course, free from proteïd, have lost their toxicity. The alcoholic extract of the muscles of some dogs was, however, poisonous, of others not. W. D. H.

Toxicity of Serum. By A. Charrin (*Compt. rend. Soc. Biol.*, 1890, 697).—A preliminary note regarding the toxicity of the serum from cases of uræmia, confirmatory of the conclusions in the preceding abstract. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Vegetable Poisons on the Germination of Seeds. By C. Cornevin (*Ann. Agron.*, **17**, 433—441).—The author's experiments are arranged under the following heads:—

A. *Action of a vegetable poison on the seeds of the species producing it.*—Seeds of *Agrostemma githago*, immersed for 6, 12, 18, 24, 36, and

48 hours in a solution of saponine, and then sown in sterilised soil, germinated sometimes as well as, and sometimes better than, untreated seeds. Similar results were obtained with seeds of *Cytisus laburnum* plunged in a solution of cytisine; in fact, more of the treated seeds germinated than of the untreated.

B. *Action of a vegetable poison not localised in the seed on the seeds of the plant producing it.*—Poppy seeds contain no poisonous alkaloïds, and tobacco seeds no nicotine. Seeds of *Nicotiana tabacum*, plunged for 38 hours in a concentrated decoction of tobacco, and then sown, did not germinate until 48 hours after untreated seeds. Seeds sown in soil watered with dilute nicotine (1 : 50) had their germination retarded by 10—23 days, and some refused to germinate. On the other hand, of 50 poppy seeds soaked for 38 hours in aqueous extract of opium, 48 germinated, whilst only 33 out of 50 untreated seeds germinated, and this, 24 hours after the others. Out of 50 poppy seeds sown in soil impregnated with opium, 49 germinated; out of 50 sown in soil watered with water only, 35 germinated a day in arrear of the treated lot. To ascertain which of the opium alkaloïds exercises this stimulating effect on germination, solutions of morphine, narceïne, codeïne, papaverine, narcotine, and thebaïne were tried separately, with the result that narcotine, codeïne, and narceïne stimulated or hastened the germination, whilst papaverine retarded it by 24 hours, and morphine and thebaïne were without influence.

C. *Action of a vegetable poison on seeds of species not producing it.*—Maceration of 30 hours in solutions of oleandrine and of andromedotoxin (from azaleas) had no injurious effect on the germination of peas, barley, wheat, and oats; but, whereas haricots were uninjured by oleandrine, their germination was retarded 9—10 days by andromedotoxin.

Colchicine was without effect on wheat, barley, and oats, but was fatal to the germination of haricots and very injurious to that of peas.

Cytisine prevented the germination of haricots, but was without effect on wheat, oats, barley, peas, and mustard.

Saponine and nicotine prevented the germination of haricots, but were without influence on wheat. Opium appeared to hasten the germination of oats.

D. *Influence of the duration of contact of the poison on the germination of seeds.*—Immersion of wheat in nicotine solution for 30 hours was without influence, but if the action was continued for 60 hours only a few seeds germinated, and that after a retardation of 7—8 days.

Three hours immersion of haricots in cytisine was without influence; 6 hours accelerated the germination; 9 hours prevented half the seeds from germinating; 12 hours immersion was fatal to all. Nicotine and saponine take 24 hours to destroy the germinating power of haricots. Wheat is more susceptible to injury from nicotine than from cytisine or saponine; the reverse is the case with haricots. J. M. H. M.

Direct Absorption of Ammoniacal Salts by Plants. By A. B. Griffiths (*Chem. News*, **64**, 147; compare Müntz, Abstr., 1890,

79, 287).—Bean seedlings, after immersion in copper sulphate solution to destroy nitrifying microbes, and washing with sterilised water, were allowed to grow under antiseptic conditions in a sterilised solution containing 0·1 per cent. of potassium chloride, 0·003 per cent. of ferrous carbonate, and 0·05 per cent. of sodium chloride, ammonium, calcium, and magnesium sulphates, and tricalcium phosphate.

At the end of four weeks, the ammonia in the culture solution had diminished to an amount corresponding with 0·027 per cent. of ammonium sulphate. There had been no direct absorption of atmospheric nitrogen, for nodules were not formed on the roots or rootlets, and there had been no nitrification, for at no time could any traces of nitric nitrogen be found in the culture solutions; hence the ammonium salts must have been directly absorbed by the plant. Jn. W.

Mineral Substance in Teak. By D. Hooper (*Zeit. Kryst. Min.*, **19**, 485, from *Nature*, **37**, 523).—The inorganic matter of teak (*Tectona grandis*) was formerly determined as $CaHPO_4$. The author finds that the inclusions of a tree from Nilambur have the following composition:—

$CaCO_3$.	$Ca_3(PO_4)_2$.	Quartz.	Organic matter.	H_2O.
70·05	2·89	9·76	14·33	3·00

B. H. B.

Composition of the Ash of Achyranthes aspera, Linn. By C. J. H. Warden (*Chem. News*, **64**, 161).—The ash, which is used in India as an alkali, for washing, dyeing, and medicinal purposes, contains potassium salts equivalent to 21·5 per cent. of potassium oxide in the leaves, to 38·0 per cent. in the stems, and to 28·6 per cent. in the roots. The author suggests the use of the plant as a cheap green manure. Jn. W.

Starch in the Fungus Boletus pachypus, Fr. By E. Bourquelot (*J. Pharm.* [5], **24**, 197—199).—The occurrence of starch has been very rarely detected in fungi. Thin sections of the foot and cap of *B. pachypus* stained with iodine solution give a blue coloration, due to the presence of starch in the tissue. The liquid pressed out of the fungus does not give the starch reaction. On boiling the fungus with water, the filtered solution gives a precipitate with alcohol, which, when redissolved in water, gives a blue coloration with iodine solution; a second portion mixed with fresh saliva (diastase solution) loses its property of becoming blue with iodine solution after a short time, whilst a third portion, treated with saliva and kept at the laboratory temperature for 10 hours, acquires the power of reducing alkaline copper solution. J. T.

Formation and Physiological Significance of Oxalic Acid in Fungi. By C. Wehmer (*Ann. Agron.*, **17**, 462—464; from *Bot. Zeit.*, 1891, **15**).—The author has experimented with pure cultivations of fungi in nutritive solutions. In doses of 1 per cent., oxalic acid is fatal to the growth of fungi, but in smaller quantities it is assimilated and decomposed by some as carbonaceous aliment in default of any

more suitable. Fungi form oxalic acid from any sort of carbonaceous compound which they can assimilate; its formation depends less on the nourishing medium and the species grown than on the degree of development which the fungus attains; it is, however, directly promoted by the presence of bases in the solution with which it can combine. The quantity formed is often many times greater than that of the fungus itself, and the weight of oxalic acid *plus* fungus corresponds nearly with that of the sugar consumed when sugar is used as nutritive medium. The author looks on oxalic acid as the product of incomplete respiration, and its persistence is, to a great degree, determined by the presence of bases. It is destroyed by further oxidation, with production of carbonic anhydride and water. J. M. H. M.

Organic Acids in Beet Juice. By E. O. v. Lippmann (*Ber.*, **24**, 3299—3306).—The presence of malic and tartaric acids in beet juice, hitherto asserted without proof by the text-books, has been proved. The chalk precipitate formed when unripe beets are treated in the evaporating apparatus contains, besides oxalic and citric acids, small quantities of lævomalic, dextrotartaric, and glutaric acids. Some deposits were also examined which had been formed in the preliminary warming of the juice after its treatment with chalk. One contained, besides oxalic acid, ordinary succinic and normal adipic acids. Another contained, besides oxalic, glycollic acid; about the same time as this was deposited, it was noticed in the factory that a white powder sometimes separated out during the filtration of the juice; this powder was shown to contain a polymeride of glyoxal. The author has once succeeded in obtaining glyoxylic acid from quite young beet plants. The presence in beet juice of the first five members of the oxalic acid series has now been proved, and also of glycollic, glyoxylic, malic, tartaric, and citric acids. C. F. B.

Constituents of Henbane Seed. By F. Ransom (*Pharm. J. Trans.* [3], **22**, 215—216).—The author obtained from the dried seeds of biennial plants of *Hyoscyamus niger*, grown at Hitchin, only 0·058 per cent. of alkaloïd. The seed is, therefore, not so rich in alkaloïd as some have asserted, and as it contains also much fixed oil, in which the alkaloïd is to some extent soluble, its use for galenical preparations seems undesirable. R. R.

Alkaloïds of the Solanaceæ. By W. Schütte (*Arch. Pharm.*, **229**, 492—531).—The author summarises the conclusions to be drawn from his paper, thus:—

(1.) The younger roots of wild belladonna contain only hyoscyamine, whilst the older roots contain atropine as well as hyoscyamine, but only in small proportion; the same was observed to be the case in the older cultivated roots.

(2.) The ripe berries of cultivated *Atropa belladonna nigra* contain atropine and hyoscyamine; those of the wild plant contain atropine only; the ripe fruit of *Atropa belladonna lutea* contains only atropine, and another base, perhaps identical with atropamine. The unripe

fruit of wild *Atropa belladonna nigra* contains hyoscyamine with only a small quantity of atropine.

(3.) The leaves of the yellow and black fruited, wild *Atropa belladonna* contain hyoscyamine and atropine, the latter being in small quantity only.

(4.) Fresh and old seeds of *Datura stramonium* contain chiefly hyoscyamine; small quantities of atropine and scopolamine are also present.

(5.) *Solanum tuberosum* contains, besides betaïne, an alkaloïd which causes mydriasis.

(6.) The mydriatic alkaloïd contained in *Lycium barbarum* and *Solanum nigrum* exists only in small quantities, and appears to be identical with the base contained in *Solanum tuberosum*.

(7.) The leaves of *Nicotiana tabacum* also contain traces of mydriatic alkaloïds.

(8.) In the seeds, leaves, and root of *Anisodus luridus*, gathered in autumn, hyoscyamine only has a pre-existence. A. G. B.

Toxic Principles of Amanita pantherina, D.C. By Inoko (*J. Pharm.* [5], **24**, 261—262; after *Pharm. Post*, **24**, 1891, 581; compare R. Böhm, Abstr., 1885, 1008).—The fungus, when dried, loses a portion of its poisonous activity. A dried sample yielded 0·1 per cent. of alkaloïds, consisting of choline with a little muscarine.

J. T.

Cicuta maculata, Linn. By R. Glenk (*Pharm. J. Trans.* [3], **22**, 69—70).—This paper contains the results of a complete analysis of the fruit of *Cicuta maculata*, with the chemical reactions of the volatile oil, resins, an aqueous extract, and the constituents of the ash. The author obtained an alkaloïd which, however, does not occur in the root also, but was unable to determine whether or no this was coniine, owing to insufficiency of material. At one stage of the operations a strong coniine-like odour was noticed. R. R.

Pollen of Pinus Sylvestris. By K. Kresling (*Arch. Pharm.*, **229**, 389—425; compare von Planta, Abstr., 1886, 91).—The methods adopted in the analysis of the pollen were those recommended by Dragendorf. Full details are given in the original paper; the results are summarised as follows:—

Moisture, 8·73 per cent.

Ash, crude ash, 5·51 per cent.; pure ash, 3·0 per cent., containing:—

K_2O.	Na_2O.	MgO.	CaO.	P_2O_5.	SO_3.	Cl.	Fe_2O_3.	Al_2O_3.	SiO_2.	Mn_2O_3.
37·16	1·62	4·94	4·63	28·70	4·38	1·35	4·08	1·86	10·51	trace.

(Compare Famintzin and Przybytek, *Bull. Acad. Imp. Sci. St. Pétersbourg*, **30**, 358.)

Fat, 11—12 per cent., melting about 40°, and containing:—glycerol, 5·24 per cent.; alcohols, chiefly cholesterol and myricyl alcohol, 6·16 per cent.; fatty acids, 87·85 per cent., of which 77·35 per cent. is oleïc acid, and 22·65 per cent. solid acids, chiefly palmitic.

Lecithin, 0·895 per cent.

Cane sugar, 12·75 per cent.

Starch, 7·4 per cent.

Total glucose, obtained by boiling with seminormal acid, 33·1 per cent., which is 11·7 per cent. more than can be accounted for by the cane sugar and starch; this remainder must be derived from the carbohydrates of the cell wall.

Cellulose, 19·06 per cent.

Mucilage, 0·196 per cent.

Organic Acids.—Tartaric and malic acids were isolated. Five grams of pollen gave sufficient acid to neutralise 17 c.c. of decinormal sodium hydroxide solution.

Nitrogenous Compounds.—Globulin, nucleïn, peptone, albumin, amines, and ammonia (0·094 per cent.) were detected. No peptonising ferments were found. Proteïds, soluble in water and precipitated by tannin, 1·61 per cent. By extraction with dilute hydrochloric acid and sodium hydroxide, 1·595 per cent. of proteïds was dissolved and precipitated by tannin. After this extraction there is still 0·681 per cent. of nitrogen, calculated on the original pollen, in the residue, and about half the total of nitrogen, namely, 1·34 per cent., remains in the extract, not being precipitated by tannin. Of bases, there were isolated: xanthine, 0·015 per cent.; guanine, 0·021 per cent.; hypoxanthine, 0·085 per cent., and a small quantity of a substance rich in nitrogen, vernine. A. G. B.

Rain as a Source of Nitrogen for Vegetation. By C. F. A. Tuxen (*Forsch. Gebiete Agr. Phys.*, **14**, 367—368; from *Tidsskr. f. Landökon.*, 1890, 325—350).—In connection with the question of the nitrogen compounds at the disposal of plants, the nitrogen compounds of rain in Denmark were investigated. The tables on the next page show (I) the amount of rain (from 1880 to 1885) and the ammonia and nitric acid per million; and (II) the amount of nitrogen as ammonia and as nitric acid in kilograms per hectare.

The ammonia is chiefly due to the decomposition of organic matter. The results are considered to be high, as the rain was collected near a rather large village, where the production of ammonia and nitric acid would probably be greater than in other parts of the country.

N. H. M.

The Phosphoric Acid of the Soil. By P. P. Dehérain (*Ann. Agron.*, **17**, 445—454).—The author discusses the assimilation of phosphoric acid by different crops in the light of facts furnished by the experimental plots at Grignon.

The plots left unmanured since 1875 gave, of late years, very poor crops, and the author has attributed this result, in great measure, to the impoverishment of the soil in humus. As regards the direct elements of fertility, he has shown that the nitrogen is still easily nitrifiable, and that the total phosphoric acid is as much as 0·1 per cent. Yet a dressing of 200 kilos. mineral superphosphate on this plot raised the yield of wheat in 1890 from 8 to 22 metric quintals per hectare, whilst 200 kilos. of superphosphate with 200 kilos. of potassium chloride gave 24 metric quintals. Even then, as regards wheat,

I.

	Summer.			Autumn.			Winter.			Spring.		
	Rain-fall.	Ammo-nia.	Nitric acid.	Rain-fall.	Ammo-nia.	Nitric acid.	Rain-fall.	Ammo-nia.	Nitric acid.	Rain-fall.	Ammo-nia.	Nitric acid.
	mm.			mm.			mm.			mm.		
1880-1	141	0·75	0·40	287	0·85	0·46	78	3·38	0·80	76	1·80	0·50
1881-2	178	0·70	0·45	184	2·53	0·15	74	4·36	0·03	103	3·07	0·16
1882-3	215	0·81	0·31	165	1·71	0·13	61	7·98	0·04	47	9·90	0·12
1883-4	179	1·50	0·44	205	1·05	0·04	173	1·05	0·31	98	3·63	0·56
1884-5	146	0·92	0·85	173	0·58	1·26	114	5·10	1·09	88	4·35	2·01

II.

	Summer.		Autumn.		Winter.		Spring.		Whole year.		
	Ammo-nia.	Nitric acid.	Ammo-nia.	Nitric acid.	Ammo-nia.	Nitric acid.	Ammo-nia.	Nitric acid.	Ammo-nia.	Nitric acid.	Total nitrogen.
1880-1	1·06	0·56	2·38	1·27	2·71	0·62	1·31	0·35	7·46	2·80	10·26
1881-2	1·24	0·82	4·82	0·28	3·14	0·02	3·13	0·16	12·33	1·28	13·61
1882-3	1·79	0·68	2·91	0·22	4·81	0·03	3·96	0·05	13·47	0·98	14·45
1883-4	2·71	0·80	2·21	0·08	1·78	0·53	3·63	0·56	10·33	1·97	12·30
1884-5	1·38	1·20	0·98	2·15	5·60	1·11	3·46	1·61	11·42	6·07	17·49

the sterility is largely due to exhaustion of assimilable phosphoric acid, the total phosphoric acid, nevertheless, remaining abundant. The author long since proposed to treat samples of soil with acetic acid in order to distinguish the assimilable from the non-assimilable phosphates, on the assumption that the calcium phosphate of the soil is assimilable and entirely soluble in acetic acid, the ferric and aluminium phosphates being non-assimilable and insoluble. In point of fact, the soil of the unmanured plots yields only traces of phosphate soluble in acetic acid, whilst that of the manured plots yields notable quantities, as do other soils on which dressings of superphosphate produce no increase of crop. The soil of the unmanured plots contained, in 1879, 0·03 per cent. of P_2O_5 soluble in acetic acid, to-day, only traces; in 10 years, therefore, a layer of soil weighing 4000 tonnes per hectare has lost 1200 kilos. of assimilable P_2O_5. The crops removed during this time certainly contained less than 400 kilos. of P_2O_5 altogether, so that two-thirds of the assimilable P_2O_5 must have been washed out of the soil or converted into inert forms. The former alternative is improbable, drainage waters, especially from unmanured soils, containing mere traces of phosphoric acid. As regards the second alternative, Thénard concluded long ago, that a dressing of calcium phosphate (bone black) was converted, after a time, into ferric and aluminium phosphates by reaction with soil, and the same thing may be proved by a laboratory experiment. If a little calcium phosphate be mixed with soil and treated with carbonic acid water in a seltzogene, after a few days it is found that no phosphate is dissolved, although calcium phosphate by itself is soluble in carbonic acid water. The soil may be replaced by oxide of iron or alumina with the same result.

Although ferric and aluminium phosphates may be non-assimilable by wheat, they appear to stand on a different footing as regards oats, for whereas the plots manured every year gave, in 1888, 37·8 metric quintals of oats per hectare, the plots unmanured since 1875 gave as much as 31·1 metric quintals. Moreover, in 1891, whilst the manured plots gave 36 metric quintals of oats, and the unmanured plots 28, the addition of 200 kilos. of superphosphate to the latter only raised the yield to 30 quintals.

The author suggests, as a possible explanation, that the acid in the juice of the roots is carbonic acid, that the roots of oats may be more charged with this than those of wheat, and that the carbonic acid may withdraw alkali carbonate from its association with the clay of the soil to form bicarbonate, which is capable of dissolving the phosphates of iron and alumina, although carbonic acid itself will not do so. Even calcium carbonate, in conjunction with carbonic acid water, is capable of causing the solution of ferric phosphate.

It is probable that dressings of farmyard manure, containing as it does alkali carbonates, assist in the solution of these phosphates, and so render them assimilable by crops, and also liable to be washed out of the soil. J. M. H. M.

Analytical Chemistry.

The Application of Capillary Phenomena to the Analysis of Liquids. By E. Gossart (*Compt. rend.*, **113**, 537—540).—Every liquid may be caused to roll in drops upon itself, the drops being separated from the main body of the liquid by a thin stratum of vapour. A drop is allowed to fall from a height of 1 mm. upon the concave meniscus at the edge of the vessel containing the liquid. It is convenient to use a vessel with sloping sides, giving a meniscus of hyperbolic section. The liquid is rendered viscous by the addition of such substances as citric acid or glycerol. Using two pure liquids, the drops of the one never roll upon the other, owing to the immediate absorption of the separating film of vapour.

If the supporting liquid contains an impurity, test drops of the same liquid will roll upon the supporting liquid, provided that they contain the same percentage of the same impurity, or that this percentage only varies within fixed limits. These limits can, with care, be reduced so far that it becomes possible to find the amount of impurity present within $\frac{1}{500}$ of the total. Each impurity behaves as if it alone were present.

A general method for the detection and estimation of impurities in liquids hence becomes possible; it is particularly serviceable in the case of spirituous liquors. W. T.

Estimation of Free Hydrochloric Acid in the Stomach. By L. Graffenberger (*Landw. Versuchs-Stat.*, **39**, 455—459).—The best method for the estimation of the free hydrochloric acid in the contents of the stomach is that of Sjöquist (Abstr., 1889, 302), as modified by v. Jaksch; this modification consists in estimating the barium gravimetrically as barium sulphate.

In the present research, the applicability of the method was tried with various artificial mixtures, to which a known amount of hydrochloric acid was added; the mixtures contained chlorides; organic acids; organic acids and chlorides; peptone; peptone, chlorides and organic acids; starch; and lastly starch, peptone, pepsin, organic acids, and chlorides. The result in all cases was the same, or at least the error never exceeded 0·01 per cent. The method is thus an admirable one. Proteïds other than peptones in the mixture give rise to a loss of acid of from 3 to 4 per cent. W. D. H.

Estimation of Chlorates. By F. A. Gooch and C. G. Smith (*Amer. J. Sci.* [3], **42**, 220—223).—The authors communicate a rapid and easy but indirect process for the estimation of chloric acid, which is briefly as follows:—An accurately measured solution containing potassium iodide, sodium hydrogen arsenate, and dilute sulphuric acid is boiled in an Erlenmeyer's flask until the liberated iodine is expelled. The residue, after cooling, is first neutralised with soda, then mixed with excess of solution of sodium hydrogen carbonate,

and finally titrated with N/10 iodine. The experiment is now repeated, this time with the addition of a definite amount of a chlorate. As there is no reaction between hydriodic acid and arsenic acid, as long as there is a chlorate present, the amount of iodine used to reoxidise the arsenious acid will be considerably less. The amount of chloric acid may, therefore, be readily calculated. It is of great importance to have a good excess of potassium iodide. The test analyses are satisfactory. L. DE K.

Microscopic Detection of Sulphurous Anhydride. By G. DENIGÉS (*J. Pharm.* [5], **24**, 289—290).—A saturated solution of cadmium nitrate is diluted with 20 vols. of an aniline solution containing 20 to 25 grams per litre. Immediately before use a little of this is acidified with about 1 per cent. of acetic acid, taken up on the end of a glass rod, and held over the mouth of the vessel from which sulphurous anhydride is supposed to be escaping. In presence of this compound, a white film rapidly forms, which, under the microscope, is clearly seen to consist of regular, hexagonal plates. If the cadmium solution is not acidified, the test appears to be more sensitive, but, under the microscope, the hexagonal crystals are found to be almost completely replaced by far less characteristic radiating crystals. J. T.

New Method of Estimating Nitrogen. By E. BOYER (*Compt. rend.*, **113**, 503).—The method is founded on the complete reduction of nitric nitrogen to ammonia by oxalates and sulphur in presence of soda-lime. A reducing mixture is made, consisting of 1 part of sulphur, 2 parts of calcium oxalate, and 6 parts of soda-lime. A quantity of the dry substance containing not more than 0·5 gram of nitrate is intimately mixed with 50 grams of the reducing mixture. A combustion-tube, 55 cm. long and 1·7 cm. in diameter, is closed at one end, and is then charged by the successive introduction of 2 grams of calcium oxalate, 10 grams of powdered soda-lime, 10 grams of the reducing mixture, the substance mixed as above, 10 grams of the reducing mixture, 10 grams of powdered soda-lime, and a plug of asbestos. The combustion is carried on just as in an ordinary soda-lime combustion, and occupies about 40 minutes. It is necessary to boil the standard sulphuric acid, before titration, to expel the sulphuretted hydrogen and carbonic anhydride formed during the combustion.

The method may be employed to determine total nitrogen existing in the three states of organic, ammoniacal, and nitric nitrogen, and yields good results; for instance, an analysis of sodium nitrate gave 16·45 of nitrogen for 16·47 present; a mixture containing 0·1284 gram of organic and ammoniacal nitrogen yielded 0·1281 gram; a mixture containing burnt leather, ammonium sulphate, and sodium nitrate gave 0·1161 gram nitrogen out of 0·11655 gram; a similar mixture containing dried blood yielded 0·1624 gram out of 0·1627 gram of nitrogen present. W. T.

Estimation of Carbon in Steel. By A. A. BLAIR (*Chem. News*, **64**, 66—69; from *J. Anal. and Appl. Chem.*, **5**, 3).—A continuation

of the work of the International Steel Standards Committee; certain modifications are recommended in the ordinary combustion process.

The double chloride of copper and potassium is to be preferred to the analogous ammonium salt, as the latter is liable to contain organic impurities derived from the manufacture of the ammonia.

The air used for the combustion is best supplied from a pressure-cylinder, as the use of an aspirator facilitates the introduction of impurities from the atmosphere of the laboratory.

The products of combustion are best purified by cuprous chloride and anhydrous copper sulphate, the former absorbing the free chlorine, the latter the hydrogen chloride; the cuprous chloride, which is converted into a convenient granular form by heating the moistened powder and stirring until dry, is placed in the anterior limb of a Marchand U-tube, the posterior limb of which is occupied by the copper sulphate, guarded by a plug of asbestos. As anhydrous copper sulphate is a more efficient desiccating agent than the granular calcium chloride used in the guard-tube of the potash bulb, it is necessary to moisten the gases as they leave the purifying apparatus, and dry them again over calcium chloride before they enter the absorption apparatus. For this purpose, a plug of cotton wool placed in the bulb of a Marchand U-tube containing the calcium chloride is moistened at the commencement of each combustion.

In weighing the potash-bulbs, the use of capillary stoppers is recommended, as they allow the equalisation of pressure without permitting the introduction of any sensible amount of moisture.

Jn. W.

Estimation of Thallium. By H. Baubigny (*Compt. rend.*, **113**, 544—547).—The estimation of this metal by precipitation as thallous iodide admits of accurate results, notwithstanding the remarks of previous observers. The inaccuracy of the method alleged by Willm is due to the final washing with distilled water. Werther's assertion that thallous iodide is insoluble in ammoniacal water is not borne out by the facts, but its solubility in dilute alcohol is less than that author indicates. The most accurate modification of the process is carried out as follows:—The thallous iodide is precipitated at 80—90°, it then collects together well without to any extent adhering to the glass. The whole is cooled; the orange precipitate, at first very finely divided, forms a dense, crystalline, yellow powder which may be readily filtered. The precipitate is washed with a 1 per cent. solution of potassium iodide, in which it is insoluble, until free from foreign salts; finally the potassium iodide is washed out by 82° alcohol, which, while readily dissolving potassium iodide, does not dissolve enough thallous iodide to yield even a coloration with ammonium sulphide after concentration of the washings to one-fifth their bulk. The precipitate is dried and detached as completely as possible from the filter, and in order to avoid the use of a tared filter, the thallous iodide adhering to the paper is dissolved by the aid of a little dilute nitric acid, and received in a tared porcelain crucible; the solution is then gently evaporated with a few drops of hydrochloric acid, precipitated by the addition of a drop of concentrated hydriodic acid, dried, the main quantity of the precipitate added, the whole heated for some hours at 170°,

and weighed. Although thallium and its salts are too volatile to allow of the incineration of the paper without loss, thallous iodide does not volatilise at 170°. Test analyses gave accurate results. (Compare Long, Abstr., 1891, 1295.) W. T.

Oxidation of Copper-glance by the Electric Current. By E. F. Smith and D. L. Wallace (*Ber.*, **24**, 2938—2939; see also *Ber.*, **23**, 2276).—It has been shown that metallic sulphides in alkaline solutions are decomposed by the electric current in such a way that the whole of the sulphur is oxidised to sulphuric acid. Copper-glance was the only exception. The authors have now succeeded in completely decomposing this mineral by the electric current.

Finely powdered copper-glance (0·1068 gram) and potassium hydroxide (35 grams) are mixed in a nickel crucible and submitted for 40 minutes to the action of an electric current producing 1 ampère of electrolytic gas per minute. Before stopping the current, it is reversed for a few minutes. The contents of the crucible are then washed out with water, filtered from the insoluble oxide, acidified with hydrochloric acid, and precipitated with barium chloride. The results are good: 20·80 and 20·91 per cent. of sulphur being obtained, as against 21·00 per cent. obtained by oxidation with nitric acid.

The essential conditions for success are the employment of a large quantity of potassium hydroxide and the prolonged action of the electric current. E. C. R.

Electrolytic Separation of Mercury from Copper. By E. F. Smith and A. W. MacCauley (*Ber.*, **24**, 2936—2938).—The authors have found that by carefully regulating the current, the separation of mercury from copper is complete, even when the latter is present in twice as large a quantity as the former. Moreover, the presence of zinc, nickel, or other metals in no way hinders the separation. A table of the results obtained is given. E. C. R.

A Reaction for Cerous Oxide. By P. C. Plugge (*Arch. Pharm.*, **229**, 558—561).—The most delicate reagent for cerous oxide is a solution of 1 part of strychnine in 1000 parts of concentrated sulphuric acid. The suspected solution is made alkaline with sodium hydroxide, evaporated on a piece of porcelain, and the dry residue brought in contact with 2 or 3 drops of the strychnine solution; in the presence of cerium, a bright-blue colour is developed which rapidly fades and gives place to a cherry-red or pale-red, according to the quantity of cerium present. As little as 0·01 milligram of cerous oxide can be detected in this way, the colour being a pale blue-violet which rapidly disappears.

This test was devised for the detection of cerium in the contents of a stomach, where the cerium was present in the form of oxalate, which is officinal in some pharmacopœias as a remedy for vomiting, dyspepsia, &c.; in such a case, the presence of sodium hydroxide is necessary to decompose the cerium oxalate. The test may also be applied directly to a precipitate produced by ammonia and contain-

ing zinc and aluminium as well, only ammonium sulphide or zinc sulphide must not be present. A. G. B.

Separation of Manganese and Nickel, Manganese and Cobalt, and of Manganese, Nickel, and Cobalt. By P. Jannasch and C. J. Franzek (*Ber.*, **24**, 3204—3205).—It has been previously shown by Jannasch and McGregory (Abstr., 1891, 963) that zinc and manganese may be quantitatively separated by means of hydrogen peroxide in strong ammoniacal solution and in presence of a large quantity of ammonium chloride. The separation of manganese from nickel may be readily carried out under similar conditions, but not that of manganese and cobalt. If, however, the hydrogen peroxide is added to these metals when in the form of double alkali cyanides, the manganese precipitate is completely free from cobalt; in the same way manganese may be separated from nickel, or, as would be expected, from a mixture of both these metals. The precautions necessary to ensure success will be published later. H. G. C.

Volumetric Estimation of Iron by Potassium Dichromate and Stannous Chloride. By R. Namias (*Gazzetta*, **21**, 473—476).—The author considers the ordinary method of estimating iron by dichromate, using potassium ferricyanide as an indicator, to be inconvenient and somewhat inexact. He finds the following method to give good results:—An excess of standard dichromate solution is run into the solution of the ferrous salt, acidified with hydrochloric acid; a few drops of iodine and starch solution are added, and the excess of dichromate determined by titration with standard stannous chloride solution.

It is convenient to use a potassium dichromate solution containing about 5 grams of the salt per litre; the stannous solution should be equivalent to this. W. J. P.

Colorimetric Estimation of Iron. By L. Lapicque (*Compt. rend. Soc. Biol.*, 1890, 669—671).—In view of certain observations by Krüss and Morath (Abstr., 1889, 124), in which they found the colorimetric estimation of iron led to variable results, the author has re-examined his former method (Abstr., 1890, 297) of estimating the iron in blood. He also finds certain variable factors, but by using a large excess of alkali thiocyanate in constant proportion, and then acidifying strongly with sulphuric acid, these are reduced to a minimum. Among the circumstances leading to variation, temperature must be mentioned; to obviate this, it is suggested that every time a series of estimations is to be made, the thiocyanate should be previously titrated with a ferric salt in order to determine the constant K. W. D. H.

Decomposition of Chrome-Iron Ore by Hydrochloric Acid under Pressure. By P. Jannasch and H. Vogtherr (*Ber.*, **24**, 3206—3208).—The method already recommended by one of the authors for decomposing silicates, namely, by heating with hydrochloric acid under pressure in a platinum apparatus (Abstr., 1891,

619), may also be adopted with advantage in decomposing chrome-iron ore for quantitative analysis. The most suitable acid is a mixture of 4 vols. of concentrated acid of sp. gr. 1·119 and 1 vol. of water, and it should be saturated with ammonium chloride; the tubes must be heated for 8—10 hours at about 250°, the decomposition being then at least as complete as with the methods usually adopted.

H. G. C.

Estimation of Molybdic and Tungstic Acids. By E. F. Smith and R. H. Bradbury (*Ber.*, **24**, 2930—2936).—The authors have made experiments to determine if molybdic and tungstic acids can be estimated by means of their barium, calcium, strontium, lead, silver, cobalt, bismuth, or cadmium salts. The following results were obtained:—

Barium molybdate is precipitated on adding barium chloride to a cold solution of sodium molybdate. It dissolves completely in acids, is more soluble in a dilute solution of ammonium nitrate than in water, and dissolves in 17,200 parts of water at 23°. The quantitative estimation was carried out as follows:—A measured quantity of sodium molybdate solution containing 0·1144 gram of molybdenum was made up to 200 c.c., heated to boiling, precipitated with a boiling solution of barium chloride, allowed to remain until cold, filtered, washed with cold water, and the precipitate separated from the filter-paper, and ignited. The results obtained were good. If the precipitate be filtered while the solution is hot, a small quantity of molybdenum will be found in the filtrate.

Barium tungstate is a heavy, white precipitate, which is decomposed by warm acids with formation of yellow tungstic acid, and is more soluble in dilute ammonium nitrate than in water. The quantitative estimation, which gives good results, is carried out in a similar way to the molybdate, but in this case the precipitate is collected while hot, and washed with hot water.

Strontium molybdate resembles the barium salt in appearance, is practically insoluble in water, dissolving in 9600 parts at 17°. It is easily decomposed on heating, and is, therefore, not suitable for quantitative estimations.

Strontium tungstate behaves in the same way as the molybdate.

Calcium Molybdate.—The addition of calcium chloride to a cold, dilute solution of sodium molybdate does not cause a precipitate. On adding alcohol, or on heating the solution to boiling, a white, granular precipitate is at once obtained, which is somewhat soluble in water, and insoluble in alcohol. The quantitative estimation was carried out in the same way as for the barium salt, but although the filtrate contained molybdenum, the results were always too high. The following method was then employed:—The calcium molybdate was precipitated in boiling solution, and boiled until the precipitate became granular, cooled, one-third the volume of alcohol added, the mixture allowed to remain for some time, filtered, and the precipitate washed with dilute alcohol (1 : 3). The filtrate contained no molybdenum. On heating the precipitate in a platinum crucible to a strong, yellow heat, it loses weight, and, unless the heating is sufficient, high results are obtained.

Calcium tungstate resembles the preceding salt, but the quantitative results varied considerably.

Lead molybdate is a white, granular precipitate, in a moist condition soluble in nitric acid and sodium hydroxide; on heating, it acquires a yellow colour, and then is not attacked by the above reagents. With regard to the quantitative results, the authors confirm the results of previous observers.

Lead tungstate is a white, flocculent, finely-divided precipitate, extremely hard to filter, and insoluble in water. It is quite insoluble in ammonium nitrate, and the addition of this salt renders the filtration much easier. The quantitative results were good.

Silver tungstate and molybdate are at once precipitated on adding silver nitrate to solutions of the sodium salts. Silver tungstate is more finely divided and more difficult to filter than the molybdate. The latter is a white precipitate resembling silver chloride, distinctly soluble in water, easily soluble in nitric acid, potassium cyanide, and sodium hydroxide; on heating, it turns purple, and melts at a low temperature to a clear, yellow liquid. Silver tungstate is yellow, less soluble in water, melts at a higher temperature, and, on heating, turns dark-purple. These salts are not suitable for quantitative experiments, as they are soluble in water, and decompose on heating.

Cadmium molybdate is a heavy, granular salt, insoluble in water, and, when moist, soluble in ammonia, acids, and potassium cyanide, and, after heating, is still soluble in acids. Good quantitative results are obtained as follows:—The solution is precipitated with cadmium nitrate, collected on a Gooch's porcelain crucible, and, after drying, carefully heated.

Cadmium tungstate is obtained in a fine state of division, but is not difficult to filter. It resembles the molybdate, but, after heating, is not soluble in acids. The quantitative estimation is carried out in the same way as for the molybdate.

The authors point out that probably an estimation of molybdic and tungstic acids when mixed could be obtained by dividing the solution into two parts: in one part estimating the mixed acids as cadmium salts, and in the other part also precipitating as cadmium salts, then dissolving in potassium cyanide, and determining the cadmium electrolytically.

The bismuth salts are insoluble in water.

Cobalt molybdate is not formed either in cold dilute or concentrated solutions. By heating a concentrated solution of sodium molybdate with cobalt nitrate, a small quantity of a bluish-white precipitate is formed, which dissolves again on cooling.

Cobalt tungstate is violet-red, and is at once formed on adding cobalt nitrate to a solution of sodium tungstate. E. C. R.

Estimation of Antimony and its Condition of Oxidation. By F. A. Gooch and H. W. Gruener (*Amer. J. Sci.* [3], **42**, 213—220).—When antimonious oxide is treated with iodine in an alkaline solution, it passes into the higher state of oxidation. If, on the other hand, an acid solution of antimonic oxide is boiled with hydriodic

acid, iodine is liberated, and the antimony is reduced to the lower state of oxidation.

On these principles the authors have based the following process for the determination of antimony:—A weighed quantity of the antimony salt, corresponding with about 0·2 gram of Sb_2O_3, is titrated in presence of 1 gram of sodium tartrate and 20 c.c. of a saturated solution of sodium hydrogen carbonate, with N/10 iodine solution standardised against tartar emetic. The result of this titration gives the amount of Sb_2O_3. 4 grams of tartaric acid is then added to the liquid, and, if still alkaline, dilute sulphuric acid is added until the mixture is neutral. 10 c.c. of 50 per cent. sulphuric acid is now added, and also a little over a gram of potassium iodide. The liquid is diluted to 100 c.c., and boiled in an Erlenmeyer flask until the volume is reduced to 50 c.c. In order to prevent bumping, a platinum spiral is introduced, and to obviate mechanical loss, also a trap made of a two-bulb drying tube, cut short, and hung, large end downward, in the mouth of the flask. The faint colour still remaining after concentration is bleached by means of centi-normal sulphurous acid, and the solution nearly neutralised with sodium hydroxide; 20 c.c. of solution of sodium hydrogen carbonate is again added, and the liquid once more titrated with the standard iodine solution in the presence of starch. This titration gives, of course, the entire amount of antimony present. The difference between the indications of the two titrations gives the antimony in the higher state of oxidation. The process is accurate and rapid, as shown by many test analyses, and also extremely simple as regards manipulation. L. de K.

Carbazole Method for Estimating Nitrates in Water Analysis. By W. P. Mason (*Chem. News*, **64**, 197).—The author, who is slightly disappointed with the delicacy and uniformity of results obtained by this process, points out the fact that cold solutions darken much more slowly than the warmer ones. In applying the process, the same precaution must be taken as when nesslerising for ammonia, namely, the standards and the solutions of unknown strength must be operated on at the same temperature. After the addition of strong sulphuric acid, the tube may be cooled immediately, or gradually, before the carbazole solution is added. The latter solution, which in a stoppered flask keeps for about 48 hours, acts best when its colour has changed to an olive-green. L. de K.

Estimation of Nitrates in Water. By A. Hazen and H. W. Clark (*Chem. News*, **64**, 121—122, and 162—164).—The authors have examined the phenolsulphonic acid process of Grandval and Lajoux (Abstr., 1885, 1093), and find that it is not trustworthy, as the various nitrophenols which may be formed have colouring powers differing in intensity.

The aluminium process, however, yields more satisfactory results. 50 c.c. of the water is treated with 2 c.c. of 40 per cent. sodium hydroxide solution and 0·4 gram of aluminium foil, 0·12 mm. thick, and the whole is allowed to remain at the ordinary temperature for 24 hours. If the free ammonia is high, it must be distilled off before

adding the aluminium. A portion of the solution, varying from 1 to 25 c.c., according to the amount of nitrates present, is now diluted to 500 c.c. with water free from carbonic anhydride (prepared by passing steam through distilled water), and nesslerised in the usual way. It is found unnecessary, in most cases, to distil before nesslerising, as the water is sufficiently decolorised and clarified by the action of the hydrogen. The diluent water must be free from carbonic anhydride, as otherwise the liquid will become turbid with precipitated aluminium hydroxide. A correction is made for the volume of the sodium hydroxide solution, the ammonia carried off by the hydrogen, and the ammonia converted into nitrogen, the factor being 0·88 when the above quantities are used. The authors have experimentally determined the amount of ammonia carried off by the hydrogen, and find it to agree with the amount calculated from the gaseous laws. Albuminoïd matter is attacked by the hydrogen, part of it being converted into an amount of ammonia varying from 2 to 4 per cent. of the albuminoïd ammonia, but the quantity is negligible unless the latter is very high. Jn. W.

Estimation of Volatile Oil in Copaiba. By R. A. Cripps (*Pharm. J. Trans.* [3], **22**, 193—194).—In a small weighed flask, 0·5 gram of copaiba is placed with about 5 c.c. of water. A regulated jet of steam is sent through the mixture, and, as the exit tube from the flask leads into a test tube immersed in cold water, any turpentine present can be immediately recognised by its odour. The exit tube is provided with a bulb, in which any resin mechanically carried over is arrested. In half an hour, the loss of weight, after drying the flask at 100°, represents all the volatile oil. R. R.

Examination of Spirits for Secondary Constituents. By A. H. Allen and W. Chattaway (*Analyst*, 1891, 102—115).—The authors have devised the following process (a modification of Marquardt's method) for the estimation of fusel oil in commercial spirits, such as whisky:—As a preliminary step, any fixed matters must be removed, and any ethers and furfuraldehyde destroyed. 100 c.c. of the spirit is taken, 20 c.c. N/10 soda added, and the whole heated in a reflux apparatus for an hour. The contents of the flask are then distilled in the following manner:—A volume of 90 c.c. is allowed to pass over, the flame is then removed, and 30 c.c. of water is introduced into the distilling flask. The distillation is conducted until 20 c.c. more has been collected. The flask is allowed to cool, and 10 grams of sodium sulphate washed into it with 20 c.c. more water. If now the distillation be continued until another 20 c.c. has passed over, all the amyl alcohol will have been volatilised. The entire distillate is now diluted with brine until the density of the liquid is about 1·1, when it is shaken four times successively with carbon tetrachloride, using 40 c.c. the first time, then 20 c.c., and lastly, 10 c.c. The carbon tetrachloride now contains the amyl alcohol (and other fusel constituents), and, probably, some ethyl alcohol, which may be removed by agitation, first with brine, afterwards with a strong solution of sodium sulphate. The oxidation of the fusel oil may be

conducted in a closed bottle, or, more conveniently, using a reflux condenser. The oxidising mixture consists of 5 grams of potassium dichromate, 2 grams of strong sulphuric acid, and 10 c.c. of water. When a flask is used attached to a reflux condenser, the carbon tetrachloride should be kept in active ebullition for eight hours, the source of heat being a water-bath. After oxidising, the product is diluted with 30 c.c. of water and distilled over a naked flame until only 20 c.c. remains in the flask. 80 c.c. of water is now added, and the distillation continued until only 5 c.c. remains in the flask. The distillate will now contain the whole of the valeric acid, a portion being dissolved in the carbon tetrachloride, and the remainder in the aqueous fluid. The entire distillate is now titrated with N/10 barium hydroxide, using methyl orange as an indicator, and shaking thoroughly after each addition. If the carbon tetrachloride has, before use, been well purified by treatment with the oxidising mixture and redistillation, no more than 2 c.c. of the baryta solution ought to be required. Phenolphthaleïn is now added, and the titration continued, with frequent shaking, until the neutral point is again reached. Each c.c. of N/10 alkali used in the second stage of the titration corresponds with 0·0102 gram of valeric acid or 0·0088 gram of amyl alcohol. The neutralised aqueous fluid is now carefully separated from the carbon tetrachloride (which can be used again), evaporated to dryness at 130°, and the residual barium salt is weighed. After allowing for any barium chloride, which may be calculated from the alkali used in the first stage of the titration, the mean combining weights of the organic acids can be found as follows:—

$$\frac{\text{Milligrams of organic barium salt}}{\text{c.c. of N barium hydroxide}} \times 67{\cdot}5 = \text{combining weight of organic acid.}$$

The process gives very accurate results, providing the following points are rigidly observed:—

1. The carbon tetrachloride must be previously purified by treatment with chromic acid mixture and subsequent distillation over barium carbonate, and must be free from chloroform.

2. All corks used in distilling the spirit must be kept distinct from those employed in the distillation of the products of oxidation. They must be always carefully covered with tin-foil.

3. A few small fragments of pumice-stone should be added, in each case, to the contents of the distilling flasks. They should be treated with the chromic mixture before use.

4. The brine should be made from clean table salt, and rendered distinctly acid with sulphuric acid.

Qualitative and Quantitative Estimation of Furfuraldehyde.—Furfuraldehyde in spirits can be detected, and its proportion roughly guessed at, by the reaction of the sample with a solution of aniline in glacial acetic acid. Ten drops of aniline are dissolved in 2 c.c. of the acid, and the mixture added to 10 c.c. of the spirit to be tested. A red coloration, which increases in intensity after a time, shows the presence of furfuraldehyde. If a quantitative estimation is required, the authors proceed as follows:—

200 c.c. is distilled to about 20 c.c., when 50 c.c. of water is added, and the distillation continued until all but 10 c.c. has passed over. The distillates are mixed and divided into two equal parts, A and B. One portion, A, is titrated with N/10 soda, using phenolphthaleïn as indicator, and the free acid thus found calculated to acetic acid. The neutral liquid is treated with 20 c.c. of N/10 soda and boiled in a reflux apparatus for one hour, when the excess of alkali is ascertained by titrating with N/10 hydrochloric acid. The other portion, B, is treated with 1 c.c. of aniline and 1 c.c. of phosphoric acid of 1·442 sp. gr., and boiled in a reflux apparatus for at least two hours. It is then distilled to a low bulk, and the distillate neutralised and treated with 20 c.c. of N/10 soda, exactly as was done with the other portion. The difference between the alkali added and that found by titration represents that consumed by the saponification of the ether in 100 c.c. of the spirit; each c.c. represents 0·0088 gram of ethylic acetate.

The difference between the amounts of alkali required for the saponification of portions A and B represents the alkali which has reacted with furfuraldehyde, acetaldehyde, &c. Assuming only the first to be present, 1 c.c. of N/10 soda represents 0·0192 gram of furfuraldehyde.

One of the authors very much questions whether the presence of even an excess of amyl alcohol in whisky constitutes a danger to health. L. DE K.

Estimation of Glycerol, Astringent Acids, and Colouring Matter in Wine. By F. JEAN (*Analyst*, 1891, 56—57).—*Estimation of the Glycerol.*—250 c.c. of the sample is evaporated to the volume of 100 c.c., agitated with lead oxide, and then rendered slightly alkaline with baryta-water. The filtrate is neutralised with dilute sulphuric acid, concentrated to about 50 c.c. in a flat porcelain dish, and mixed with 5 grams of lead oxide, 10 grams of sand, and 20 grams of barium sulphate. The mass is cautiously dried at 100°, and the powdered residue extracted with a mixture of equal parts of alcohol and ether until the liquid measures 60 c.c. 30 c.c. is placed in a tared glass capsule, and 20 grams of dry litharge having been added, the whole is evaporated on the water-bath, and then dried to a constant weight at 105—106°. The other 30 c.c. is evaporated in a tared glass capsule of 6 cm. diameter, and finally dried in an air-bath at 160—170°. The difference in weight between residue No. 1 (after allowing for the litharge) and No. 2, multiplied by 8, and divided by 1·243, gives the number of c.c. of glycerol in 1 litre of wine.

Estimation of Astringent Acids.—(*a.*) *Œnontannin.* 250 c.c. of the sample is concentrated down to 100 c.c., shaken with excess of freshly precipitated arsenious sulphide, and then filtered. The filtrate is concentrated to 50 c.c., mixed with 10 grams of silica and 20 grams of barium sulphate, and finally dried at 100°. The residue is powdered and extracted with warm ether; the latter is evaporated, and the residue is dissolved in a little alcohol. Into this solution is now introduced a weighed quantity of dry, prepared, powdered hide, which will take up all the tannin in about half an hour. After

washing it with spirit, it is dried at 100° and reweighed. The increase in weight, multiplied by four, equals the œnontannin in 1 litre of the wine. (*b.*) *Œnogallic Acid.* The alcoholic filtrate is diluted with distilled water up to 100 c.c., and in 20 c.c. of this, the acid is estimated by means of a solution of iodine, previously standardised with gallic acid, as follows :—Two solutions are prepared, one containing 0·2 gram of iodine per litre, the other 0·125 gram of gallic acid in 250 c.c. of distilled water. Into a beaker, marked 50 c.c., is put 10 c.c. of the gallic acid solution and 3 c.c. of a saturated solution of sodium hydrogen carbonate. Iodine solution is now added from a burette until a drop of the mixture, tested on thick filter-paper dressed with powdered starch, leaves a stain surrounded by blue. Water is now added up to the mark, and iodine again added until a similar stain is obtained. Having thus standardised the iodine, it is used in a similar manner on the 20 c.c. of the alcoholic liquid, mixed with 3 c.c. of solution of sodium hydrogen carbonate. (*c.*) *Colouring matter.* 250 c.c. of the sample is slowly evaporated down to 100 c.c., rendered alkaline with ammonia, and shaken up with freshly-precipitated arsenious sulphide. After filtering, a slight excess of acetic acid is added, and the liquid once more filtered. The two filters containing the arsenious sulphide are, after washing, heated with spirit slightly acidified with acetic acid, which gradually dissolves out the colouring matter. The alcoholic solution is evaporated in a tared capsule, desiccated at 105°, and the residual colouring matter is weighed. L. DE K.

Estimation of Pentoses in Vegetables. By W. E. STONE (*Ber.*, **24**, 3019—3021).—The material under examination is heated in a retort with hydrochloric acid (sp. gr. 1·06) so that not more than 10 c.c. of distillate is obtained in five minutes, fresh acid being added from time to time. As soon as the distillate ceases to react with aniline acetate, the heating is suspended, and the distillate neutralised with soda, slight excess of acetic acid added, and the liquid diluted with water to a known volume. Portions of 25 c.c. are then mixed with phenylhydrazine solution, quickly boiled, rapidly cooled, and filtered, the filtrate being tested with alkaline copper solution; if it contains excess of phenylhydrazine, less is added in subsequent titrations; after three or four experiments, it is possible to determine the exact quantity of phenylhydrazine required, within 0·1 c.c.

The phenylhydrazine solution is made by dissolving 1 gram of phenylhydrazine hydrochloride, and 3 grams of sodium acetate in 500 c.c. of water, and is standardised by titration with a solution containing 1 gram of pure furfuramide and a little acetic acid in 1 litre of water. The phenylhydrazine solution changes after 24 hours.

Although this method does not give results which are theoretically correct, since part of the material is decomposed during distillation with the acid, the numbers obtained for the same substance are uniform, and the percentages of pentoses contained in different alimentary substances can be readily compared. J. B. T.

Estimation of Mixtures of Saccharose, Invert Sugar, and Dextrose or Levulose. By G. Wiechmann (*Analyst*, 1891, 15—33).—A direct estimation of saccharose in presence of dextrose and levulose has been proposed by Winter. This process, the accuracy of which is much doubted by the author (but which wants further investigation), is carried out as follows:—The sugar solution is mixed with a solution of lead acetate, to which ammonia has been added until a permanent precipitate threatens to form. An abundant white precipitate is formed, which is then digested with a large amount of water. The filtrate contains the sugar as a lead compound, from which the lead may be readily separated by a current of carbonic anhydride. The insoluble portion is suspended in water, and also treated with carbonic anhydride to liberate the dextrose. The insoluble mass, which still contains the levulose, will yield the latter on treatment with hydrogen sulphide.

Indirect processes, based on polarisation, do not always yield accurate results, as the polarimetric observations are too much influenced by a small change in temperature.

The author, who has made a large number of test analyses (without making any important alteration in the process), has proved the accuracy of the method proposed by Sieben, which is based on the following principle:—

The saccharose and dextrose + levulose are calculated from the copper-reducing power before and after inversion. Any levulose, whether naturally present, or formed from half the quantity of the saccharose during inversion, may be readily destroyed by prolonged boiling with excess of hydrochloric acid, and subequently determined from the diminished copper-reducing power. L. de K.

Estimation of Maltose, Dextrose, and Dextrin in Beer-wort and Beer by means of Ferment Organisms. By H. Elion (*Chem. Centr.*, 1891, ii, 281; from *Centr. Bakteriologie u. Parasitenkunde*, **9**, 525—528).—The author refers again to this method (Abstr., 1891, 368), and in proof of its validity, he points out that the reducing power of the sugar which disappears during fermentation and the amount of dextrose formed by hydrochloric acid from the same, almost exactly corresponds with the amount of maltose. At the same time, he admits that under the term "maltose" he includes also any other sugar which may have undergone fermentation, still the result is sufficiently exact for technical purposes. The author also objects to the use, as in Bau's experiments (*loc. cit.*), of *Saccharomyces apiculatus*, since its nature and fermenting qualities have not as yet been sufficiently examined. J. W. L.

Estimation of Cholesterol. By K. Obermüller (*Zeit. physiol. Chem.*, **16**, 143—151).—In the estimation of cholesterol in mixtures containing neutral fats, the sodium ethoxide method of saponification (Abstr., 1890, 1474) is found to cause no loss of cholesterol.

W. D. H.

Carbohydrates. By B. Tollens and others (*Landw. Versuchs-Stat.*, **39**, 401—453).—In the analysis of vegetable products by the usual

method, the fat, proteïds, insoluble fibre, and ash are estimated directly, and the difference between the sum of these components and 100 is returned as "extractive matter free from nitrogen." This extractive matter consists for the most part of carbohydrates, which can be estimated directly by means of Fehling's solution, after previous treatment with dilute acids; it contains, however, in many cases, a considerable proportion of substances which cannot be estimated in this manner, and for the detection and estimation of which suitable methods are greatly needed.

In the present paper, the author reviews the most important reactions of various carbohydrates, with reference to the analysis of vegetable products in general.

The levulinic acid reaction is first discussed, and it is stated that the formation of this acid, on boiling a substance with hydrochloric acid of sp. gr. 1·09—1·10 for 20 hours, may be considered as strong evidence of the presence of a true carbohydrate* (compare Wehmer and Tollens, *Annalen*, **243**, 315; Abstr., 1888, 535). The following substances give the levulinic acid reaction:—Cane sugar, dextrose, levulose, inulin, gum-arabic, filter-paper, fir-wood, starch, Carragheen moss, levulin, lactose, galactose, raffinose, irisin, mannose, sorbin, the glucosides salicin and amygdalin, potato-juice, and chondrin. It must be borne in mind that even in the case of a true carbohydrate only a small quantity of levulinic acid is formed, and that the isolation of the acid is by no means an easy matter; consequently an unsuccessful attempt to obtain the levulinic acid reaction only shows the absence of any considerable quantity of a true carbohydrate.

Having ascertained in this way the presence of a true carbohydrate, its isolation and identification have next to be considered.

In the case of dextrose, or of substances such as lactose, raffinose, salep-juice, &c., which yield dextrose, the presence of this sugar can be easily proved by oxidising the substance with nitric acid (compare Gans and Tollens, *Annalen*, **245**, 215; Abstr., 1888, 1059); the formation of saccharic acid under these conditions is a proof of the presence of dextrose, or of dextrose-groups. Inulin, sorbin, arabinose, galactose, mannose, and quince-juice† do not give the saccharic acid reaction.

The formation of mucic acid on oxidation with nitric acid (compare Creydt and Tollens, Abstr., 1886, 582) may be taken as a proof that a substance contains galactose or galactose groups; it has been shown that this acid is obtained from galactose, lactose, raffinose, and Carragheen moss, and also from the "sulphite-liquors" of the wood-cellulose process (compare Weld, Lindsay, Schnelle, and Tollens, Abstr., 1891, 43). The quantity of raffinose in molasses can, in fact, be determined by estimating the mucic acid produced on oxidation (compare Creydt, Abstr., 1887, 307). There is no reaction by which the presence of levulose, or of levulose groups, in a vegetable product

* *Note by Abstractor.*—The term "true carbohydrate" seems to apply only to the hexoses, and to compounds such as starch, inulin, &c., which yield hexoses on hydrolysis.

† *Note by Abstractor.*—Quince-juice, according to Bauer (see p. 128), yields dextrose on hydrolysis.

can be satisfactorily determined; the readiness with which this sugar undergoes decomposition on heating with sulphuric acid, or dilute hydrochloric acid, yielding brown solutions, may, however, serve as a means of distinguishing it from dextrose; Seliwanoff's colour reaction (Abstr., 1887, 459) is also to be recommended in particular cases.

Mannose can be readily detected by warming a dilute solution of the substance under investigation with phenylhydrazine acetate; its presence is shown by the formation of a crystalline hydrazone (m. p. about 188°). As this sugar is usually present in vegetable products in a combined form, the substance must first be heated with 3 per cent. hydrochloric acid for some hours. The presence of mannose in the "sulphite-liquors" from the wood-cellulose process is easily proved by means of the phenylhydrazine reaction; the sugar can be conveniently prepared by decomposing the hydrazone with concentrated hydrochloric acid.

The pentoses, arabinose, and xylose, although closely related to the hexoses, differ from the latter in possessing certain characteristic properties by which their presence in a given vegetable product can be easily proved. They do not give the levulinic acid reaction, but when distilled with hydrochloric or sulphuric acid they yield a distillate which contains furfuraldehyde; the presence of this compound can be easily ascertained by the red coloration which is produced on the addition of aniline or xylidine (compare Schiff, Abstr., 1887, 571). As, however, the hexoses give traces of furfuraldehyde under the same conditions, the presence of pentoses must not be regarded as definitely established unless the reaction is very marked, or unless the furfuraldehyde is determined quantitatively by means of phenylhydrazine (compare Chalmot and Tollens, Abstr., 1891, 768). The pentoses also give a characteristic red colour with phloroglucinol and with orcinol, in presence of hydrochloric acid. It must be borne in mind that glycuronic acid and its derivatives give all the reactions of the pentoses.

A very complete account of the occurrence, properties, and methods of estimation of the pentoses is given, but all the principal facts dealt with have formed the subject of previous papers by the author and others (compare Abstr., 1891, 43, 659, 768). F. S. K.

Valuation of Oil of Cloves. By H. Thoms (*Pharm. J. Trans.* [3], **22**, 450, 451).—Assuming that the quantity of eugenol in oil of cloves can be taken as a measure of the value, the author proposes to separate the eugenol directly from the oil in the form of benzoyleugenol, by mixing the oil with solution of sodium or potassium hydroxide, and then adding an equivalent of benzoic chloride. Crystalline benzoyleugenol separates as the mixture becomes cold, is recrystallised several times from hot alcohol, washed with alcohol at 17°, and weighed dry on a filter, allowance being made for its solubility (0·55 gram in 25 c.c. of 90 per cent. alcohol). From the weight of benzoyleugenol, the quantity of eugenol present in the oil can be calculated. R. R.

Examination of Vinegar. By W. J. Sykes (*Analyst*, 1891, 83—87).—The author thinks that considerable information may be gathered from an examination of the nitrogenous constituents of a vinegar, as to whether it is genuine or not; but the fixing of limits must naturally be reserved until a long series of experiments have been performed in this particular direction.

Albumoses may be estimated by precipitation with a saturated solution of ammonium sulphate. Peptone may be precipitated in the filtrate by the cautious addition of a solution containing 4 grams of tannin in 190 c.c. of proof spirit mixed with 8 c.c. of dilute acetic acid. Pure malt vinegar should also give a turbidity with phosphotungstic acid, or potassium bismuth iodide, or potassium mercuroiodide. L. de K.

Adulteration of Beeswax. By A. and P. Buisine (*Bull. Soc. Chim.* [3], **5**, 654—660).—Amongst the substances used to adulterate beeswax, the most conspicuous and common are those indicated in the accompanying table. Although the influence of some of these on the physical character of the wax is extremely marked, others, by judicious selection, can be so combined as to imitate it, not only in its physical characteristics, but also in its behaviour under the methods of analysis at present in use.

The authors propose, in addition to the usual estimation of free and combined fatty acids, to determine the unsaturated fatty acids, the free hydrocarbons, and the alcohols present in the sample, as well as its melting point and density.

The sample, dried at 110°, at which temperature it should not lose more than 1 per cent. of its weight, should leave no residue of mineral adulterants on treatment with hot chloroform or turpentine. The melting point and density of the original sample should correspond with those of beeswax. Any serious adulteration will be rendered evident by this procedure, and will necessitate further examination to determine its nature and amount. To estimate the soluble fatty acids, an excess of which indicates the presence of vegetable waxes, and to detect soluble colouring matter such as turmeric and annatto, 20 grams of the sample is extracted with hot water. The dried residue is utilised for the determination of the free and total fatty acids, the unsaturated acids (by iodine absorption), the alcohols (by the amount of hydrogen liberated by alkalis), and the free hydrocarbons.

The nature and approximate amount of the adulterants are then determined, in the manner already indicated, by reference to the appended table (see next page), which embodies the results obtained by the examination of the various adulterants known to be in use.

Jn. W.

	Melting point.	Density.	Soluble acids in milligrams of KHO per gram of sample.	Free acids in milligrams of KHO per gram of sample.	Total acids in milligrams of KHO per gram of sample.	Iodine absorption per 100 parts of sample.	C.c. of hydrogen at 0° and 760 mm. yielded by 1 gr. of sample.	Hydrocarbons per 100 parts of sample.
Japanese wax	47—54°	—	2	18—28	216—222	6—7·55	69—71	0
Chinese wax.....	53·5	—	2	22	218	6·85	72·3	0
Vegetable waxes	47—54	—	2	17—19	218—220	6·6—8·2	73—74	0
Carnauba wax	83—84	—	0	4—6	79—82	7—9	73—76	1·6
Mineral waxes.....	60—80	—	0	0	0	0—0·6	0	100
Paraffins.....	38—74	—	0	0	0	1·7—3·1	0	100
Suint wax.....	62 - 66	—	0	95—115	102—119	13—18·5	0	14—18
Fatty acids of suint.....	50 -62	—	0	155—185	159—189	2 6—2·8	0	0
Tallow	42—50·5	—	0	2·75—5	196—213	27—40	52—60	0
Stearic acid	55·5	—	0	204	209	4	—	0
Resin.....	—	—	0	168	178	135·6	35	0
Yellow beeswax.....	62—64	—	0—1	19—21	91—97	8—11	53—57·5	12·5—14·5
White beeswax	63—64	0·962—0·967	0—2	20—23	93—110	2—7	53—57	11—13·5

General and Physical Chemistry.

Measurement of Light Intensity by the Expansion of Chlorine. By A. Richardson (*Phil. Mag.* [5], **32**, 277—284).—The author has confirmed Budde's observation (*Phil. Mag.*, 1871) that when chlorine is exposed to sunlight an expansion of the gas occurs, which is independent of direct heating effects due to the light; and that the volume to which the gas first expands is maintained during exposure, provided that the intensity of the light remains constant, contraction to the original volume taking place when the gas is shaded.

In order to compare the expansion obtained in this way with the light intensity, as determined by means of a Bunsen and Roscoe's pendulum actinometer, a differential apparatus was constructed, consisting of two tubes of 55 c.c. capacity and 10 cm. in length, which were connected with a graduated horizontal gauge, provided with a small bulb at each end. The gauge and bulbs contained strong sulphuric acid, a short column of air serving as index. The tubes to be exposed were suspended in a box, which could be placed at any required angle to face the sun, and when filled with dry air were found to be equally heated. One tube was then filled with dry chlorine, and the acid, up to the index, was saturated with this gas. The bulbs containing the acid were in all cases protected from the light. When the maximum expansion of the chlorine was reached at any one time, as shown by the index remaining stationary, the light intensity was measured. A comparison of the numbers thus obtained showed that the change in volume of the chlorine is very nearly proportional to the actinic intensity of the light, as given by the actinometer.

Experiments were also made with mixtures of chlorine and air. The effect of dilution with air is at first very marked, diminishing after a time, but finally increasing when only a small proportion of chlorine remains. It was found that the expansion of chlorine by light is unaffected by change of temperature within a range of from 14° to 138°.

The author finally constructed an automatic registering apparatus for measuring light intensity. This was done by suspending a differential apparatus on the beam of a balance in such a manner that the flow of acid from one arm to the other produced a movement of the beam, which was communicated by means of a lever to a pen, and was recorded on a rotating drum. This instrument will record continuously the actinic intensity of the light under all conditions of weather throughout the year. J. W.

The Application of Ketteler's Formulæ to Optical Chemistry. By R. Nasini (*Rend. Acad. Linc.*, **6**, ii, 324—331).—The author compares Ketteler's formula, $M = (n^2 - 1)(v - \beta)$ (Abstr., 1889, 326),

with those of Lorenz and Lorentz, Gladstone and Landolt, and points out that the constants β and M vary much in value under different conditions of temperature and pressure. Thus, for α-bromonaphthalene, the value of β between 16·5° and 28·1° is 0·03226, between 28·1° and 77·6° 0·15966, and the mean value between 16·5° and 77·6° is 0·13620, the numbers being for infinite wave-length. A small change in the index of refraction makes an enormous difference in the values of β and M, and as the index of a substance varies somewhat with different samples, each as pure as possible, the values calculated for β and M are very discordant, and hence of little value in optical chemistry. Ketteler's formulæ, although of great theoretical interest from a purely physical point of view, cannot be advantageously applied to optical chemistry, simply because the experimental data are not sufficiently exact. W. J. P.

Rotatory Power of Silk. By L. Vignon (*Compt. rend.*, **113**, 802—804).—Silk may be expected to act on polarised light, as it readily yields leucine and tyrosine on hydrolysis. Attempts to find a suitable solvent for the material as a whole proving unsuccessful, the two chief constituents were examined separately.

The colouring matter of the silk of *Bombyx mori* having been extracted by repeated treatment with hot alcohol acidified with hydrochloric acid, the skein is plunged into cold 3 per cent. aqueous soda solution, which dissolves the enveloping material, but leaves the matrix or fibroïn untouched. The rotatory power of a yellowish, limpid solution thus obtained was $[\alpha]_j = -39·2°$.

To prepare the fibroïn for examination, the silk is boiled twice with 10 per cent. soap solution, the soap being washed away with water after each boiling; it is then washed with acidified water (0·1 per cent. of hydrochloric acid), and finally with alcohol. The white substance thus obtained is dried and dissolved in moderately strong hydrochloric acid. A clear, dilute solution prepared in this way showed a rotatory power of $[\alpha]_j = -40°$, which was not materially altered by further dilution, or by the addition of excess of ammonia.

The rotatory powers of the two chief constituents of silk are, therefore, practically identical, and are of the same sign as those of the proteïds. Jn. W.

Changes of Voltaic Energy of Alloys during Fusion. By G. Gore (*Phil. Mag.* [5], **32**, 27—31).—Regnauld (*Chem. News*, **38**, 33) observed that liquid gallium is electropositive to solid gallium in a neutral solution of gallium sulphate. The author has made corresponding observations with various alloys. A glass dish and a tobacco pipe with a wide bowl were partially filled with a conducting liquid (solution of hydrogen chloride or sodium chloride), and connected by means of a siphon. A rod of the solid alloy was placed in the cup, and a second portion was melted in the bowl of the pipe. Connection was made through a galvanometer by means of iron wires. The alloy in the bowl was alternately heated and cooled, the galvanometer being observed in order to ascertain if there was any deflection of unusual magnitude when the temperature passed the melting point

of the alloy. As most of the alloys employed did not melt sharply, no very sudden deflection was noted, but in the case of an amalgam of 1 part of cadmium and 4 parts of mercury in a solution of sodium chloride, there was a sudden reversal of the current when the amalgam completely liquefied, the liquid being electronegative to the solid at this point. J. W.

Electromotive Forces of Metallic Salts. By C. L. Speyers (*Amer. Chem. J.*, **13**, 472—486).—In continuation of previous work (Abstr., 1890, 843), the difference of potential between mercury and copper, iron, and tin has been measured in various electrolytes in ten different states of concentration, varying from molecular proportion (gram-litre) to $\frac{1}{512}$ molecular proportion, each solution having one-half the concentration of the preceding. The metals were used in the state of amalgam wherever practicable. In the case of copper, the electrolytes were hydrochloric, nitric, acetic, and sulphuric acids, alone and in pairs; the copper salts of these acids, with the exception of the chloride, which attacked the mercury; pairs of these salts, namely, nitrate with acetate and sulphate, and acetate with sulphate; mixtures of the salts with acids, namely, the nitrate, acetate, and sulphate with nitric, acetic, and sulphuric acids; and, finally, the zinc salts of the same acids. In the case of iron, the same series of electrolytes was used, with the addition of the metallic chlorides, ferrous and ferric salts being substituted for copper salts. In the case of tin, the electrolytes used were the above acids, alone or in pairs; the chlorides, alone, or mixed with acids; the above-mentioned zinc salts, and the corresponding ferric salts.

The general conclusions which the author deduces from the numerous data thus obtained are: That the electromotive force increases, as a rule, with dilution; that in solutions containing hydrochloric acid it is lower than in those containing the other acids, and is not materially affected by the admixture of those acids or of metallic salts; that in solutions containing different pairs of metallic and acid radicles it is only slightly greater than in the solutions of the pair yielding the lower value; and that it is lessened by substituting copper, stannous tin, or, in the case of chlorides, ferrous iron for hydrogen, but is practically unaffected by the substitution of stannic tin.

The increase of electromotive force with dilution may be explained by means of the dissociation hypothesis, if the assumption is made that the mean free path of the ions is increased by dilution, so that the ions have less influence on one another, and give up, therefore, more electricity to their respective electrodes.

A theory of chemical affinity, which is proposed, is based on the non-conductivity of the non-metals. The atoms of these are supposed to contain a constant amount of negative electricity, neglecting artificial surface charges, whilst the metallic atoms contain positive, or both positive and negative, electricity, the total quantity, however, being constant. When an atom of a non-metal comes in contact with a metal, its charge attracts the positive charge of the latter, and, as it cannot unite with it, a portion of the metal is detached, and a com-

pound formed, the stability of which depends on the completeness of the internal insulation of the negative ion and the magnitude of the positive charge of the positive ion. This explains the weakness of the combinations of metals with metals, and non-metals with non-metals, and the strength of those of metals with non-metals.

The lowering effect produced on the electromotive force by stannous tin, and to a less general extent by ferrous iron, may be explained in accordance with the above hypothesis, by supposing that the negative electricity in the non-conducting ion is inextricably entangled with the matter. The initial action of the ion on the metal is to dislodge and combine with a portion of the latter containing unit positive charge, and a molecule of an *ous* compound is formed; this, however, meets with more negative ions, and gives up part of its positive charge to one of them, so that 2 molecules of the *ic* compound are formed. Since the negative electrode is charged with negative electricity by the negative ions, and partially discharged by the positive ions, it follows that when the *ic* compound is present, the charge removed is less, and the potential of the electrode numerically greater than when the *ous* compound is present. Jn. W.

Influence of Boric Acid on the Electrical Conductivity of Aqueous Solutions of Organic Acids. By G. Magnanini (*Gazzetta*, **21**, ii, 215—228).—It has been previously shown (*Gazzetta*, **20**) that the electrical conductivity of solutions of tartaric acid is sensibly increased by the addition of boric acid and is to some extent dependent on the dilution and the quantity of boric acid used; this behaviour was explained by assuming the formation of a combination of the two compounds which has electrolytic properties and is partially dissociated by water. In the present paper, the results of a series of experiments on the influence of boric acid on the electrical conductivity of aqueous solutions of acetic, benzoic, butyric, succinic, crotonic, salicylic, lactic, glyceric, gallic, amygdalic, and glycollic acids are described. There is a marked difference between the behaviour of hydroxy- and other acids, the conductivity of solutions of the former being materially increased by the addition of boric acid even in very dilute solutions; this increment rises with the quantity of boric acid added, but falls on dilution; it varies considerably with the nature of the acid under observation. Solutions of hydroxyisobutyric, pyrocatechuic, malic, and citric acids similarly show an increase of conductivity on the addition of boric acid, whilst pyruvic, dehydracetic, formic, oxalic, valeric, monochloracetic, levulinic, camphoric, and aspartic acids, which do not contain the hydroxyl group in their acid radicles, exhibit no such increase. This behaviour may possibly be of use in deciding as to the presence of an hydroxyl group in organic acids.

The electrical conductivity of aqueous solutions of resorcinol, quinol, phenol, ortho- meta- and para-cresol, guaiacol, and phloroglucinol is only very slightly increased by the addition of boric acid; on the other hand, that of solutions of catechol, and more especially of pyrogallol, is considerably increased. The author believes this to be due to the presence and position of the hydroxyl

group in these compounds, and proposes to investigate the behaviour of polyhydric phenols containing two hydroxyl groups in ortho-position in this respect. S. B. A. A.

Some Points on Electrolysis. By J. Swinburne (*Phil. Mag.* [5], **32**, 1—9).—The author considers a one-fluid reversible cell, with its external circuit closed through a resistance so high that, in comparison, the internal resistance is negligible. A coulomb passing through the cell has work done on it numerically equal to the electromotive force E. At the electrodes p and n there is chemical action, c, and local heating, h, so that as there is assumed to be no work done in overcoming the resistance of the electrolyte, $E = E_{pc} + E_{nc} + E_{ph} + E_{nh}$. The seat of E.M.F. is here supposed to be in the cell and not at the metallic junction outside.

If the chemical work is assumed to be independent of the temperature of the cell, it can be shown from the above equation that $E = E_{nc} + E_{pc} + \theta \frac{dE}{d\theta}$, when θ is the temperature (Helmholtz's equation). The author further shows how the Peltier effect at each contact in the cell can be obtained separately. When there is any secondary or "non-adjuvant" action, the cell is not reversible. The formation of lead sulphate on both plates of a secondary battery is considered by the author to be a primary reaction (that is, there is no intermediate formation of lead monoxide) and the cause of the activity of the cell.

His views of nascent action are as follows:—Sodium amalgam in dilute acid gives off hydrogen, and will reduce a ferric salt to the ferrous stage. This reduction he does not attribute to the action of "nascent" hydrogen. A better explanation would be that the metal can dissolve if it *either* reduces the ferric salt *or* evolves hydrogen. "Evolution of hydrogen and reduction of the salt are thus alternate, not consecutive, results. Similarly, in an engine, the steam either works the engine or comes out at the safety-valve; it does not begin to lift the safety-valve, and then change its mind and work the engine in a nascent state." J. W.

Relation of E.M.F. to Latent Heat, Specific Gravity, &c., of Electrolytes. By G. Gore (*Phil. Mag.* [5], **32**, 157—168).—In order to ascertain whether, in cases where the mixture or dilution of electrolytes is attended by a heat-effect, a change in the power of exciting electromotive force occurs, the author took various pairs of solutions (or one solution and pure water) at the same temperature, measured the E.M.F. of a cadmium-platinum couple in each liquid separately, then mixed the liquids, observed the temperature of the mixture, and, after allowing the liquid to acquire the former temperature, measured the E.M.F. of the couple in it. This E.M.F. he then compared with the mean value of the E.M.F. in the liquid before mixture. The results are contained in the following table. The solutions of the chlorides of sodium and potassium were measured with a zinc-platinum couple:—

Mixture.	Change of temperature in degrees centigrade.	Change in E.M.F.
Na_2SO_4 solution + dil. H_2SO_4	− 0·66	+0·0401
CH_3·COOH + water	− 0·9	+0·0730
Tartaric acid solution + water	− 0·16	+0·1923
NH_4NO_3 ,, ,, ...	− 4·44	+0·0400
$NaNO_3$,, ,, ...	− 1·42	+0·1228
$Sr(NO_3)_2$,, ,, ...	− 1·08	+0·0741
NaCl ,, ,, ...	?	+0·0668
Na_2SO_4 ,, ,, ...	− 0·14	+0·0359
$(NH_4)_2SO_4$,, ,, ...	− 0·14	+0·0402
Na_2CO_3 ,, ,, ...	− 0·28	−0·0445
KNO_3 ,, ,, ...	− 0·54	+0·0715
NH_4Cl ,, ,, ...	− 0·19	+0·0345
CH_3·COONa ,, ,, ...	+ 0·14	+0·0360
$MgSO_4$,, ,, ...	+ 0·22	+0·0787
KCl ,, ,, ...	+ 0·04	+0·1219
NaOH ,, ,, ...	+ 7·14	+0·0298
HCl ,, ,, ...	+ 2·38	+0·2872
H_2SO_4 ,, ,, ...	+11·00	+0·2375
KOH ,, ,, ...	+ 0·02	+0·0150
NH_3 ,, ,, ...	+ 0·10	+0·0040

Special experiments were also made on the contraction of salt solutions and water. The author concludes that "in cases of mere physical mixture, the changes of mean specific gravity and of mean electromotive force of electrolytes are probably related to each other as concomitant effects of the same cause, change of molecular motion."

J. W.

Specific Inductive Capacity and Latent Heat of Vaporisation. By E. Obach (*Phil. Mag.* [5], **32**, 113—127).—From a consideration of the specific inductive capacities published by Tereschin (*Ann. Phys. Chem.* [2], **36**, 792) and the heats of vaporisation observed by Schiff (*Annalen*, **234**, 338), the author finds a relation between these two magnitudes for members of various homologous series. In any one series, the quotient of the latent heat of vaporisation, λ, by the specific inductive capacity, K, is practically constant. Thus, for the ethereal salts of acetic acid the following values of λ/K are obtained :—

Methyl.	Ethyl.	Propyl.	Isobutylyl.	Amyl.
$\frac{\lambda}{K}$ 12·0	12·8	12·3	12·1	12·8

The mean value of the ratios for the corresponding formates is 9·83, and that of the benzoates, 10·33. Monatomic alcohols give a mean ratio of 7·56, and ethyl salts of the acetic series, 12·42.

The relation thus obtained in homologous series may be combined with other similar relations. For example, Trouton gives $\lambda = C\frac{T}{M}$,

where T is the boiling point in the absolute scale, M the molecular weight, and C a constant. If we make $\lambda = \gamma K$ and introduce this value in the equation, then $\gamma K = C\frac{T}{M}$, or $KM = C'T$; that is, in any series the boiling points in the absolute scale are proportional to the molecular inductive capacities. Similarly, by making use of De Heen's results, it follows that the coefficient of expansion at 0° is inversely proportional to the molecular inductive capacity.

The ratio λ/K for ethyl oxide is 20·8; for carbon tetrachloride, 21·0; for carbon bisulphide, 33·0; and for oil of turpentine, 31·1.

J. W.

Change of the Empirical and Theoretical Isothermals of Mixtures of two Substances with the Temperature. By A. Blümcke (*Zeit. physikal. Chem.*, **8**, 554—565).—The method which the author has employed in a former paper (Abstr., 1891, 375) for tracing the connection between the empirical and theoretical isothermals of mixtures is still further extended, the effect of change of temperature on the relation between the isothermals of mixtures of two substances being here considered. H. C.

Thermal Expansion of Liquid Bismuth. By C. Cattaneo (*Rend. Acad. Linc.*, **7**, ii, 88—93).—Vincentini (*Atti R. Ac. Torino*, **22**, 1886) stated that liquid bismuth has a maximum density at its point of solidification. This was contested by Lüdeking (Abstr., 1888, 790), who found the temperature of maximum density to be a few degrees above the melting point. The author confirms Vincentini's statement by observing the expansion of an amalgam of bismuth prepared by dissolving the metal in an equal weight of mercury. The experiments were conducted in dilatometers holding about 220 grams of the amalgam, those used by previous experimenters being much smaller. The saturation temperature of the amalgam was 162·7°, and the density was measured between 236° and 279°. On examining the curve obtained by plotting densities against temperatures, no breaks could be detected, the curve being practically a straight line. The author therefore concludes that liquid bismuth has a maximum density at its solidifying point. The density of liquid bismuth at various temperatures is given below:—

t.	Density of liquid Bi.	*t.*	Density of liquid Bi.
235°	10·248	260°	10·224
240	10·243	265	10·219
245	10·239	270	10·214
250	10·233	275	10·209
255	10·229	280	10·205

W. J. P.

Calculation of the Boiling Points of Normal Isomeric Ethereal Salts of the Fatty Series. By G. Hinrichs (*Compt. rend.*, **113**, 798—800).—The boiling points of the normal fatty ethereal salts having the general formula $C_pH_{2p+1}\cdot C_qH_{2q-1}O_2$ are plotted out in curves, the ordinates of which are proportional to the logarithms of the maximum moments of inertia of the molecules (*Compt. rend.*, **76**, 1592; **112**, 1128), and the abscissæ proportional to p, that is, to the length of the alkyl chains. Four different curves are thus obtained, corresponding to the four values 6, 7, 8, 9 of $p + q$, and the actual boiling points fall very fairly on them (compare Abstr., 1891, 1406, 1408, 1441; this vol., p. 2). Jn. W.

Calorimetry. By P. Mahler (*Compt. rend.*, **113**, 774—776).—The author has devised a cheap, efficient, and durable modification of Berthelot's calorimetric bomb, suitable for use in industrial and ordinary laboratories. The chief alteration is in the combustion chamber, which, instead of consisting of platinum, is made of mild steel, forged and turned to a suitable shape, and enamelled inside. The mouthpiece is closed by a screw stopper packed with a lead washer. The substance under examination is supported and ignited by apparatus attached to the stopper, and the oxygen for the combustion is supplied at a pressure of 25 atmospheres from an ordinary pressure cylinder through a stopcock screwed into the stopper. The calorimeter and agitator are constructed on the original model, with slight modifications to reduce the cost. Trial determinations of the heat of combustion of naphthalene gave good results. The apparatus is adapted for the study of furnace and other gases. Jn. W.

Thermal Constants of Active Malic Acid and Potassium and Sodium Malates. By G. Massol (*Compt. rend.*, **113**, 800—801).—The heat of solution of anhydrous malic acid is −3·31 Cal., whilst that of the monopotassium and dipotassium salts is −5·78 Cal. and +1·55 Cal., and that of the corresponding sodium salts −1·66 Cal. and +1·78 Cal. respectively.

The heat of neutralisation of the acid and of the hydrogen alkali salts is +26·23 Cal. and +12·85 Cal. with potash, +24·86 Cal. and +12·46 Cal. with soda.

The heat of formation of the solid salts from the solid acid and base, as calculated from the above data, allowing for the formation of solid water, is +29·74 Cal. and +49·15 Cal. for the monopotassium and dipotassium salts, and +22·02 Cal. and +42·12 Cal. for the corresponding sodium salts.

Dipotassium and disodium malates, prepared by neutralising the anhydrous acid with alcoholic alkali, and heating the dried products at 120° in a current of hydrogen, may be crystallised, contrary to the assertion of Kammerer (*J. prakt. Chem.*, **88**, 321), by dissolving in water, evaporating to a syrup, powdering the surface with a little of the anhydrous salt, and keeping over sulphuric acid for some months. *Dipotassium malate* crystallises in small needles, which are scattered through a firm, pasty mass. *Disodium malate* forms long, prismatic needles containing $\frac{1}{2}$ mol. H_2O. *Monopotassium and monosodium*

malates crystallise readily with 1 mol. H_2O, which is slowly lost at 120°. Jn. W.

Heat of Formation of Hydrazine and Hydrazoic Acid. By Berthelot and Matignon (*Compt. rend.*, **113**, 672—679).—Hydrazine sulphate, N_2H_4,H_2SO_4, prepared by Curtius, was employed. Heat of dissolution at 10·8° = −8·7 Cal. The heat of neutralisation was determined (1) by exact precipitation with barium hydroxide, and (2) by direct addition of dilute hydrochloric acid to the solution of the free base left after separation of the barium sulphate.

H_2SO_4 diss. + N_2H_4 diss. = N_2H_4,H_2SO_4 diss.	develops	+11·1 Cal.
H_2SO_4 sol. + N_2H_4 diss. = N_2H_4,H_2SO_4 cryst.	,,	+36·0 ,,
2HCl dil. + N_2H_4 diss. = N_2H_4,2HCl. diss.	,,	+10·4 ,,

Hydrazine is a feeble base, like ferric oxide, and its heat of neutralisation is less than that of ammonia (+12·4 Cal. per equiv.) or even hydroxylamine (+9·3 Cal.).

The heat of combustion was determined in the calorimetric bomb, the salt being mixed with a known weight of camphor.

N_2H_4,H_2SO_4 cryst. + O_2 + Aq = H_2SO_4 dil. + N_2 + $2H_2O$	develops	+127·7 Cal.

and consequently—

S (octah.) + O_4 + H_6 + N_2 = N_2H_4,H_2SO_4 cryst.	,,	+220·3 ,,
N_2 + H_4 + Aq = N_2H_4 diss.	,,	− 9·5 ,,

The formation of hydrazine is endothermic; its conversion into ammonia by loss of hydrogen and nitrogen is exothermic, and so likewise is its direct conversion into ammonia by combination with hydrogen.

N_2H_4 dil. = NH_3 dil. + N + H	develops	+25·75 Cal.
$3N_2H_4$ dil. = $4NH_3$ dil. + N_2	,,	+32·75×3 ,,
N_2H_4 dil. + H_2 = $2NH_3$ dil.	,,	+51·5 ,,

It is clear that the direct conversion of ammonia into hydrazine is not possible without the intervention of oxidising actions; but, on the other hand, the compound may be obtained by the carefully regulated oxidation of hydrogen compounds of nitrogen and the amides and nitrates derived from them, or by the reduction of oxygen compounds of nitrogen and nitro- or azo-derivatives.

It is noteworthy that the endothermic character of the nitrogen hydrides diminishes as the saturation with hydrogen becomes more complete, and this has already proved to be the case with the oxy-acids of nitrogen and the hydrides of carbon, thus: HNO dil. −28·7 Cal., HNO_2 dil. −4·2 Cal., HNO_3 dil. +14·3 Cal., and C_2H_2 −60·4 Cal., C_2H_4 −14·8 Cal., C_2H_6 +25·2 Cal.

Hydrazoic Acid.—The experiments were made with the ammonium salt supplied by Curtius. Heat of dissolution (N_3H,NH_3) at 11° =

−7·08 Cal. Heat of neutralisation by baryta +10·0 Cal., by ammonia +8·2 Cal. Hydrazoic acid is therefore comparable to amidobenzoic acid in the energy of its acid function. Heat of combustion (in the calorimetric bomb, both with and without camphor) at const. vol. = +163·8 Cal.; at const. press. +163·3 Cal.

$N_4 + H_4 = N_3H,NH_3$ cryst.	develops	−25·3 Cal.
$N_4 + H_4 = N_3H,NH_3$ diss.	„	−32·3 „
$N_3 + H + Aq = N_3H$ diss.	„	−61·6 „

Hydrazoic acid is the most endothermic of the nitrogen hydrides. It is most probably ammonia in which two atoms of hydrogen have been displaced by a molecule of nitrogen, $NH{:}N_2$, the substitution of the electronegative nitrogen for the hydrogen conferring upon the compound its acidic properties. C. H. B.

Formation of Salts in Alcoholic Solution. By C. M. van Deventer and L. T. Reicher (*Zeit. physikal. Chem.*, **8**, 536—542; compare Abstr., 1890, 553).—Continuing their investigations on the heats of formation of metallic salts in alcoholic solution, the authors have measured the heats of neutralisation of sodium and potassium ethoxides by a number of acids in the presence of an excess of alcohol. The salts formed, with the heat evolved in each case, are given in the following table:—

Sodium acetate....	7·3 Cal.	Sodium chloride ..	11·2 Cal.
Potassium acetate .	7·5 „	Sodium bromide...	12·4 „
Potassium biacetate	7·8 „	Sodium iodide.....	11·2 „
Sodium benzoate ..	6·45 „		

The authors propose to continue their investigations with other acids and bases. H. C.

Critical Temperatures of Mixed Liquids. By G. C. Schmidt (*Annalen*, **266**, 266—292).—The author has determined the critical temperatures of a number of mixtures of two liquids in order to test the validity of Pawlewski's formula $\vartheta m = \frac{n\vartheta + (100 - n)\vartheta'}{100}$ (compare *Ber.*, **15**, 460 and 2460).

In the place of the air-bath described by Galitzine (*Ann. Phys. Chem.* [2], **41**, 623), the author employed a beaker, 250 mm. in height and about 60 mm. in diameter, which was half filled with paraffin; the liquid was contained in a small sealed tube which was attached to a thermometer placed in a paraffin-bath; the temperature at which the liquid completely disappeared and the temperature at the moment of the reappearance of the meniscus were both noted. Very good results are obtained with this apparatus, but it can only be employed for temperatures below 260°, as the paraffin darkens very rapidly when heated more strongly.

The experimental values obtained in this way were in some cases rather greater, in others rather less, than those calculated by Pawlewski's formula, the maximum difference being 3·9°; as, in the

case of any particular mixture, the differences were, as a rule, either all positive or all negative, it would seem that Pawlewski's formula is not quite accurate; it is possible, however, that the deviations from the calculated values are due to a slight decomposition of one or both liquids.

The observed and the calculated critical temperatures of the mixtures are given in tables. F. S. K.

Vapour Pressure of Aqueous Solutions of Cobalt Chloride. By G. Charpy (*Compt. rend.*, **113**, 794—795).—The curve showing the variation of the vapour pressure of 32 per cent. aqueous cobalt chloride with the temperature comprises two approximately rectilinear portions, one ranging from 20° to 40°, and corresponding with the red solution, the other ranging above 75° and corresponding with the blue solution. The intermediate portion is curved. These facts point to the existence of two stable modifications of the salt, perhaps hydrates or other molecular aggregates. The curve is similar to that obtained by Étard from a consideration of the solubility of the chloride, but the intermediate limiting temperatures are not the same, those observed by Étard being 35° and 50°; this, however, is probably accounted for by the fact that he dealt throughout with saturated solutions. Jn. W.

Pressure and Specific Volume of Saturated Vapours. By C. Del Lungo (*Rend. Acad. Linc.*, **7**, i, 141—145).—The equation $\log p = k - \frac{a}{T} - b \log T$, where p is the pressure, T the absolute temperature, and a, b, and k are constants, is derived by Bertrand (*Thermodynamique*, 1887, 93) from Boyle's law and equations given by Clapeyron, Clausius, and Regnault. From the same sources the author derives the equation $\log s = k' + \frac{a'}{T} + b' \log T$, where s is the specific volume of the saturated vapour. The specific volumes of carbon bisulphide vapour at different temperatures calculated by this formula agree well to the third decimal place with the values given by Hirn. The function $p = 0$ when $T = 0$, and then increases until the critical temperature is reached, when $T = a/b$, after which it decreases indefinitely, and has no further physical significance. Similarly s is infinite when $T = 0$, and decreases to a minimum at the critical temperature, when $T = a'/b'$. For the same vapour, therefore $a/b = a'/b'$.

Zeuner's equation, ps^n = constant, where n is a constant such that $a = na'$ and $b = nb'$, may be at once deduced from the above two equations. W. J. P.

The Freezing Points of Aqueous Solutions of Boric Acid and Mannitol. By G. Magnanini (*Gazzetta*, **21**, ii, 134—141).—A study of the electrical conductivities of aqueous solutions of boric acid and mannitol has already enabled the author to determine the composition of the compound of the two substances which exists in solution (Abstr., 1890, 1357); no clue was, however, obtained to the amount of the compound produced.

An investigation of the solutions by the cryoscopic method shows that the number of molecules existing in an aqueous solution containing both boric acid and mannitol is about 5·4 per cent. less than it would be if no combination occurred, the cryoscopic constant of the solvent for water (18·5) being diminished by 5·4 per cent. in solutions containing both constituents, whilst for solutions only containing one of the substances, the constant is considerably increased in value.

The author has also determined the electrical conductivity at different temperatures (20—50°) of solutions containing boric acid and mannitol in varying proportions, and finds that the conductivity decreases by about 6 per cent., with a rise of temperature of 30° (20—50°); the rate of decrease is almost the same for differently constituted solutions. The author considers that this abnormal change in the conductivity of such solutions is only apparent, the diminution in conductivity with rise of temperature being due to increased hydrolytic dissociation. The true temperature coefficient of the electrical conductivity is, therefore, most probably positive. As a rise in temperature causes a decrease in the amount of the compound of boric acid and mannitol in the solution, the formation of this substance is probably accompanied by development of heat.

W. J. P.

The New Theories of Solution. By J. Walker (*Phil. Mag.* [5], **32**, 355—365).—This paper contains a reply to some of the objections advanced by Pickering against the theories of osmotic pressure and of electrolytic dissociation. The author doubts if Pickering's determinations of the freezing point of sulphuric acid solutions (Trans., 1890, 331) have the degree of accuracy claimed for them, and gives an example to show that the "potential dissociation" advocated by Lodge is insufficient to explain the known facts of electrolysis.

J. W.

Change of Volume on Dissolution. By J. A. Wanklyn, W. Johnstone, and W. J. Cooper (*Phil. Mag.* [5], **32**, 473—477).—When a solid dissolves in water, one of three things may happen with respect to the volume. The volume of the solution may be equal to the sum of the volumes of the dissolved substance and the water, or it may be greater, or it may be less, as is usual. When there is contraction, the authors measure it by the weight of water, which, instead of overflowing from a vessel of 100 c.c. capacity filled with water, is retained when 1 gram of salt dissolves so as to give 100 c.c. of solution. This constant they term the "condensate." In the case of sugar there is no condensate, as there is no change of volume. With some ammonium salts there is expansion, and the condensate is consequently negative. The authors state that, "in the case of very many salts, the condensate bears an atomic relation to the gram of salt which occasions it" (compare Abstr., 1891, 1412). J. W.

Mutual Solubility of Salts in Water. By J. E. Trevor (*Phil. Mag.* [5], **32**, 75—78).—With reference to Nicol's paper under the above title (this vol., p. 8), the author draws attention to the fact that the problem therein discussed has received a theoretical solution, with experimental confirmation for many cases, from the work of Nernst, Noyes, and himself. J. W.

Solubility of Mixed Crystals, especially of two Isomorphous Substances. By H. W. B. Roozeboom (*Zeit. physikal. Chem.*, 8, 504—530).—According to the rules laid down by Gibbs for equilibrium between three phases, two of which are solid salts and the other their solution, the composition of the saturated solution at constant temperature will be dependent on the pressure. Experiment up to the present has confirmed the above for a number of solutions of mixed salts, but there are a number of exceptions where the salts taken are capable of forming a double salt or an isomorphous mixture. The exception has been shown to be only an apparent one in the case of double salts by the author's investigation of the behaviour of astracanite (Abstr., 1888, 1164). Rüdorff's researches on the solubility of mixtures of isomorphous salts have, however, placed it beyond doubt that the composition of their solution is variable, and not constant, for constant pressure, even when excess of both salts is present. The explanation of this behaviour must be sought in the fact that the isomorphous salts combine with one another to form homogeneous mixed crystals, the equilibrium conditions being thus altered. This difference between isomorphous and other mixed salts is of importance, as it is evident that the solubility of mixed salts becomes a criterion of their isomorphism, but, before this property can be made any extensive use of, it will be necessary to establish the conditions of equilibrium existing between isomorphous mixtures and their solutions.

If, with Van't Hoff (Abstr., 1890, 1044), we regard isomorphous mixtures as solid solutions, the dissolution of the mixed crystals may be compared with the evaporation of a liquid made up of two components, both of which are volatile. Osmotic pressure then takes the place of vapour pressure, and, in place of the concentration of the liquid solution, that of the solid solution must be taken. If there are N molecules of the one salt, and n molecules of the second with osmotic pressure p, in the solid solution, then we get, as the expression for the law of Henry, $kp = n/(N + n)$, or, since saturation is complete when the osmotic pressure of the solid is equal to that of the solution, if the second salt is present in the solid in the molecular proportion x per cent., and if in the saturated solution the concentration is represented by c_2 molecules, then $kc_2 = x$. This, of course, assumes the absence of electrolytic dissociation. It also assumes the identity of the solid and liquid molecule, but if this is not the case, and n of the latter combine to form one of the former, the formula becomes $kc_2 = x^{\frac{1}{n}}$.

If x becomes smaller during solution and greater during the separation of the mixed crystals, the solution will be richer in the component x than the crystals. Hence, if the osmotic pressure of a saturated solution of mixed crystals increases or decreases with increasing proportion of one of the components of the mixed crystals, the ratio of this component to the other in the solution will in the one case be greater, and in the other less, than in the mixed crystals. This enables a distinction to be made of the possible cases during solution or crystallisation of mixed crystals.

If the mixed crystals are miscible in all proportions, three cases

are possible. The osmotic pressure of the saturated solution is a continuous function of the concentration, and may either increase continuously with the concentration, it may increase to a maximum and then fall, or it may fall to a minimum and then rise. In the first case, on evaporation of a solution of the two constituents, the crystals separating out would contain increasing quantities of that component the saturated solution of which had the greatest osmotic pressure, until at length nothing but a solution of this component was left. In the second case, the crystals would be of varying composition, until a point is reached corresponding with the maximum, when the composition of the crystals would be the same as that of the solution. The third case would be similar in character to the second.

If the mixed crystals are not miscible in all proportions, the osmotic pressure is no longer a continuous function of the concentration. The curve for the pressure as a function of the concentration will then be represented for a certain portion of its length by a straight line, parallel to the abscissæ axis, and terminating at one end with a certain limiting value of the concentration of the one constituent, and at the other end with a certain limiting value of the other constituent in the mixed crystals. From these end points to the points representing the pressures of the saturated solutions of the pure components, the curve may take various forms. Some of these are considered by the author, and he points out that isodimorphous mixtures probably all give a discontinuous curve of the above form.

H. C.

Solubility of Mixed Crystals of Potassium and Thallium Chlorates. By H. W. B. Roozeboom (*Zeit. physikal. Chem.*, 8, 531—535).—The author has determined the solubility of mixtures of potassium and thallium chlorates in varying proportions. He finds that these salts present one of the cases considered in a former paper (preceding abstract) of mixed crystals which are not miscible in all proportions, and obtains results which generally confirm his theoretical conclusions.

H. C.

Affinity Coefficients of Organic Acids and their Relation to Chemical Constitution. By P. Walden (*Zeit. physikal. Chem.*, 8, 433—503).—The author has determined the affinity coefficients of a large number of dicarboxylic acids from the conductivities of their aqueous solutions (see Ostwald, Abstr., 1889, 818). The values obtained for $K = 100k$ are given in the following tables:—

I. Malonic Acid and its Derivatives.

Dimethylmalonic acid...	0·076	Ethylmethylmalonic acid	0·161
Methylmalonic acid.....	0·086	Malonic acid	0·163
Isobutylmalonic acid....	0·090	Diethylmalonic acid	0·74
Butylmalonic acid	0·103	Diallylmalonic acid	0·76
Propylmalonic acid	0·112	Benzylethylmalonic acid.	1·46
Isopropylmalonic acid...	0·127	Dibenzylmalonic acid ...	4·1
Ethylmalonic acid	0·127	Chloromalonic acid.....	4·0
Benzylmalonic acid	0·151	Benzyltartronic acid	0·55
Allylmalonic acid.....	0·154		

II. Succinic Acid and its Derivatives.

(*a.*) *Mono-substitution Compounds.*

Succinic acid.....	0·0068	Isobutylsuccinic acid..	0·00882
Isopropylsuccinic acid..	0·0075	Propylsuccinic acid ...	0·00886
Ethylsuccinic acid.....	0·0085	Benzylsuccinic acid ...	0·0091
Methylsuccinic acid....	0·0086	Allylsuccinic acid.....	0·109

(*b.*) *Di-substitution Compounds.*

Antidimethylsuccinic acid	0·0123	Parabenzylmethylsuccinic acid	0·0219
Paradimethylsuccinic acid	0·0191	μ-Benzylmethylsuccinic acid	0·0247
μ-Ethylmethylsuccinic acid.....	0·0201	Parabenzylethylsuccinic acid.....	0·0262
Parethylmethylsuccinic acid	0·0207	μ-Benzylethylsuccinic acid	0·0414
Paradiethylsuccinic acid	0·0245	Paradiphenylsuccinic acid	0·0200
Antidiethylsuccinic acid	0·0343	Antidiphenylsuccinic acid	0·026
Diethylsuccinic acid (3)	0·0386	Antidihydroxysuccinic (inactive tartaric) acid	0·060
Parallylethylsuccinic acid	0·0269	Paradihydroxysuccinic (tartaric) acid	0·097
μ-Allylethylsuccinic acid	0·0359	Dextrotartaric acid	0·097
μ-Phenylmethylsuccinic acid	0·0233	Lævotartaric acid.....	0·097
Paraphenylmethylsuccinic acid	0·0372		

(*c.*) *Tri-substitution Compounds.*

Trimethylsuccinic acid .	0·0307	Propyldimethylsuccinic acid.....	0·0551
Benzyldimethylsuccinic acid	0·0455	Ethyldimethylsuccinic acid	0·0556

III. Glutaric and Pimelic Acids and their Derivatives.

Glutaric acid.....	0·00475	Benzylmethylglutaric acid	0·0059
α-Methylglutaric acid .	0·0052	Pimelic acid:	
Paradimethylglutaric acid	0·0055	From suberone, Schorlemmer.....	0·0032
Antidimethylglutaric acid	0·0055	From castor-oil, Hell..	0·00348
Metapropylmethylglutaric acid	0·0054	From pentanetetracarboxylic acid, Perkin..	0·00345
Paradiethylglutaric acid	0·0055	Of unknown origin, Ostwald.....	0·00357
Metethylmethylglutaric acid	0·0056	β-Pimelic acid, Arth...	0·00420
β-Methylglutaric acid .	0·0059	Pimelic acid from amylene bromide:	
Parethylmethylglutaric acid	0·0059	(*a.*) Bauer.....	0·0097
Parapropylmethylglutaric acid	0·0059	(*b.*) Hell	0·0091

IV. Unsaturated Dibasic Acids.

Methylitaconic acid	0·0095	Fumaric acid	0·093
Ethylmethylmaleïc anhydride	0·0097	Methylmesaconic acid	0·094
Pyrocinchonic anhydride	0·0108	Ethylmesaconic acid	0·093
Itaconic acid	0·0120	Isopropylmesaconic acid	0·093
Benzylglutaconic acid	0·0153	Methylcitraconic acid	0·238
Glutaconic acid	0·0183	Citraconic acid	0·340
Mesaconic acid	0·0794	Maleïc acid	1·17

It will be seen that, with the exception of dimethylmalonic acid, all the di-substitution compounds of malonic acid have higher affinity coefficients than malonic acid itself. The mono-alkyl derivatives, on the other hand, have smaller coefficients than the parent acid. In the cases of succinic acid, the mono-alkyl derivatives are better conductors than the free acid, the di-derivatives better than the mono-derivatives, and the tri-derivatives better than the di-derivatives. When succinic anhydride is dissolved in cold water, the electrolyte obtained is identical with ordinary succinic acid, and no evidence of the existence of a second succinic acid is obtained. The author points out that the antidihydroxy-, antidimethyl-, and μ-ethylmethyl-succinic acids have smaller coefficients than the corresponding para-acids. It would, therefore, appear possible, although in opposition to the accepted view, that the first contain the maleïnoïd, and the second the fumaroïd, grouping. H. C.

Chemical Action at a Distance. By W. Ostwald (*Phil. Mag.* [5], **32**, 145—156).—A short glass tube of about 2 cm. diameter, closed below with parchment paper, is introduced into a small beaker. Both these vessels are filled with a solution of potassium sulphate, care being taken that the level of the liquid in the tube is higher than the level in the beaker. A rod of pure zinc is dipped into the solution in the tube, and connected electrically with a piece of platinum wire, which reaches to the bottom of the beaker. A few drops of a solution of sulphuric acid specifically heavier than the potassium sulphate solution are then carefully brought with a pipette upon the bottom of the outer vessel, so as not to come into contact with the parchment diaphragm. Hydrogen is at once evolved on the platinum, and a subsequent investigation of the solution in the inner vessel shows that a quantity of zinc has dissolved in the potassium sulphate solution as zinc sulphate. Such an action as this, where the specific solvent for a metal (here zinc) is applied at a place where it can have no direct action and yet exerts its solvent power, is termed by the author a chemical action at a distance. Many instances of similar phenomena are given. For example, gold may be dissolved in a solution of common salt, by bringing the platinum with which it is connected into contact with a salt solution saturated with chlorine. Again, if two beakers—one containing a solution of ferrous chloride, the other a solution of common salt saturated with chlorine or bromine—are connected by means of a siphon filled with salt solution and closed at

both ends with parchment paper, then on introducing platinum electrodes into the beakers and connecting them through a galvanometer, a current is at once indicated, and the ferrous chloride becomes oxidised to ferric chloride in the neighbourhood of the electrode, as may be shown by the previous addition of a little potassium thiocyanate solution.

All such reactions receive a ready explanation from the theory of electrolytic dissociation, the author laying emphasis on the fact that the description of many of the experiments made by him was completely worked out at his writing table, on the basis of this theory, before he had seen any of the phenomena in question; and that after the experiments had been performed, nothing in the description required to be altered. J. W.

Chemical Action at a Distance. By S. U. Pickering (*Phil. Mag.* [5], **32**, 478).—The author holds that a simple explanation of Ostwald's experiments (see preceding abstract) may be obtained without having recourse to the theory of free ions in solution, and that, therefore, these experiments cannot be accepted as proofs of this theory. S. U. P.

Artificial Colouring of Crystals. By O. Lehmann (*Zeit. physikal. Chem.*, **8**, 543—553).—Senarmont discovered that salt crystals may be coloured by certain organic dyes without any change in the form or homogeneity of the crystal. The author has on former occasions made similar observations with other inorganic and organic compounds, and in order to ascertain something more with reference to the conditions under which this phenomenon takes place, has now made a large number of experiments on the artificial coloration of crystals. The crystals made use of were those of certain organic acids, such as succinic, protocatechuic, and phthalic acids, and these were coloured by means of different organic dyes. The author summarises his results as follows:—

The crystals always become darker in colour than the solution from which they separate. They are usually observed to be surrounded by a lighter coloured, or even quite colourless, layer, the colouring matter being deposited with such rapidity upon the growing crystal that the slow diffusion of the dye from the more distant parts of the solution is not sufficient to make up for the decreasing concentration in the neighbourhood of the crystal.

The colouring of the crystals is in nearly all cases dichroic, a proof that the colouring matter actually enters in some way into the structure of the crystal. The remarkable rule is observed that only one of the two rays produced by double refraction is coloured, whilst the other appears to be perfectly white, the colourless ray being always the one which has undergone the least refraction.

If two colouring matters are present in the solution, the presence of the one often hinders the absorption of the other. In some cases, however, the reverse takes place, and a colouring matter which alone would not be absorbed may become so when some second colouring matter is added. Change of the solvent, or the addition of other solid or liquid foreign matter, may act in a similar manner.

Different crystals are only capable of taking up certain organic dyes, so that two compounds of perfectly similar appearance may be capable of combining the one only with one, and the second only with some other dye. This fact may obviously be made available in distinguishing crystals one from another. It may also perhaps be applicable for the purification of certain dye stuffs. H. C.

Rapid Weighing on Precision Balances by means of a Scale read by a Microscope. By A. Collot (*Bull. Soc. Chim.* [3], **6**, 98—100).—The needle of a balance carries a scale illuminated from behind the balance, and viewed by a small microscope containing a scale in the focal plane of the eye-piece. The centre of gravity of the beam may be lowered considerably, and thus the rapidity of oscillation of the beam increased materially by the aid of this device. The value of each division of the scale carried by the needle being known in centigrams and milligrams, the position of rest of the indicator is ascertained by the method of oscillations, and from its deviation from the central point the weight to be added to that in the pan is known. With a little care, weighings only take one-fourth or one-fifth as long by this method as they usually do. W. T.

A Siphon for Hot Liquids or for those Evolving Gases or Vapours. By J. C. Essner (*Bull. Soc. Chim.* [3], **6**, 19—21).—Between the two arms of the siphon a reservoir is interposed; this is filled with some of the liquid to be siphoned, and hermetically closed. When the long arm of the siphon is opened, the fall of the liquid determines a diminution in the pressure of the reservoir, and a continuous flow results. T. G. N.

Inorganic Chemistry.

Preparation of Pure Hydrogen Peroxide Solution. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 24—25).—The solution of hydrogen peroxide which results from the action of hydrochloric acid (sp. gr. 1·1) on barium dioxide is extracted by shaking with ether, and the ethereal solution is agitated with distilled water, to which it yields the dissolved hydrogen peroxide. By repetitions of this process, a pure, neutral solution corresponding with 0·8—0·9 per cent of hydrogen peroxide is obtainable, from which the dissolved ether may be eliminated by distillation under reduced pressure. T. G. N.

Preparation of Hydrobromic Acid. By G. S. Newth (*Chem. News*, **64**, 215).—By means of the following arrangement a large quantity of bromine can be rapidly converted into hydrobromic acid:—A glass tube, 7 inches long and $\frac{5}{8}$ inch in diameter, is fitted at each end with a cork carrying a piece of small tubing and a piece of stout wire. The ends of these pieces of stout wire, within the longer tube,

are joined by a spiral of platinum wire 1 inch long, and after expelling the air the spiral is heated to bright redness by an electric current; a stream of hydrogen, impregnated with bromine by bubbling through that liquid, which may be heated at 60°, is passed through the longer tube, and, as long as a slight excess of hydrogen is maintained, hydrobromic acid quite free from bromine issues from the other end, and is collected in water. There is very little danger of explosion, but to render it impossible, the small supply tube may be plugged with a little glass wool. D. A. L.

Solubility of Gases in Water. By L. W. Winkler (*Ber.*, **24**, 3602—3610; compare Abstr., 1891, 384).—In this paper the author gives in tabular form the results of experiments on the solubility of nitrogen and of oxygen in water, at temperatures ranging from 0° to 80°; the calculated values for the solubility of the two gases at temperatures ranging from 80—100° are also given. As regards the solubility of nitrogen, the author's values are considerably larger than those given by Bunsen. F. S. K.

The Densities of Sulphuric Acid Solutions. By S. U. Pickering (*Chem. News*, **64**, 311).—Lunge's doubts as to the accuracy of the author's density determinations are, in the opinion of the latter, due to a misapprehension as to the method employed to determine the strength of the acid, and as to the experimental error involved. S. U. P.

The Contraction on Mixing Sulphuric Acid and Water. By S. U. Pickering (*Chem. News*, **64**, 14—15).—From his own results the author has calculated the strength at which the maximum contraction occurs, and finds that this maximum, when calculated for unit weight of solution, shifts from 67 per cent. at 8° to 70·1 per cent. at 38°, whereas the maximum contraction calculated per unit volume remains practically constant at 76 per cent. throughout this range of temperature. Neither of these maxima occurs at the composition of the dihydrate (73·1 per cent.) or of that of any other hydrate of which indications have been obtained. The rate at which the amount of contraction is influenced by the temperature varies irregularly with the actual value of the temperature; thus with solutions from 64 to 80 per cent. strength, the contraction diminishes at nearly the same rate for the intervals 8° to 18°, and 28° to 38°, whereas for the intermediate interval, 18° to 28°, the rate of diminution is about 25 per cent. smaller. S. U. P.

Density and Composition of Dilute Sulphuric Acid. By A. W. Rücker (*Phil. Mag.* [5], **32**, 304—313).—Pickering (Trans., 1890, 64) deduced the existence of various hydrates in sulphuric acid solutions from sudden changes of curvature in the curves representing the variation of the density, &c., of such solutions with the composition. The author considers the "first differential" curve for 18° between 46 per cent. and 80 per cent., in which there are supposed to be four breaks, and shows that it is possible to find an equation, and, therefore, a continuous curve, which will represent the results within the limits of the experimental error. The equation is of the form

$$y = a + bx - cd^x + \frac{m}{n^x + n^{-x}},$$

and contains seven arbitrary constants. The author thus doubts the value of "differentiation" or of the bent ruler, as used by Pickering, in discovering changes of curvature in curves drawn to represent experimental numbers. J. W.

The Densities of Sulphuric Acid Solutions. By S. U. Pickering (*Phil. Mag.* [5], **33**, 132).—The curve used by Rücker (see preceding abstract) to bridge over four of what the writer considered to be breaks in the figure formed by the first differentials of the densities of the acid can, he maintains, prove nothing about one of these breaks, and very little about another, for it extends too short a distance beyond them. The formula for the curve suggested by Rücker consists of a combination of an exponential curve and a straight line, on to part of which (as this curve did not agree with the results) a hump was engrafted by means of a complex fourth term, the whole forming a curve for which, as an expression of physical facts, there would seem to be no precedent. The points, moreover, at which the term expressing the hump begins to be appreciable and again becomes inappreciable correspond exactly with the positions assigned by the author to two of the breaks, thus confirming, rather than disproving, the existence of these as points where some new conditions in the solutions become sensible. The only break which Rücker's curve does successfully bridge over is that particular one which the author pointed out to be especially doubtful: and even in favour of this break the evidence is not thereby entirely negatived.

The author maintains that even the most successful attempt to offer an alternative explanation of a small portion of some of his results could not upset his conclusions which were based entirely on the cumulative evidence derived from many sources, and of which he here gives a summary. S. U. P.

Boron Phosphides. By H. Moissan (*Compt. rend.*, **113**, 726—729).—*Boron phosphide*, PB, is obtained by reducing the phosphoiodide in hydrogen at 450—500°. The product is powdered, and again heated in hydrogen at the same temperature in order to remove excess of iodine, and the process is repeated two or three times if necessary, care being taken that the temperature does not exceed 500°. It is a very light, amorphous, maroon-coloured powder, insoluble in the chlorides of arsenic, phosphorus, carbon, and antimony, and in all solvents, organic and inorganic, that were tried. It is not volatile in a vacuum at 500°. At 200°, in presence of oxygen, it burns and yields boric and phosphoric anhydrides; when thrown into fused alkaline nitrates, there is incandescence and deflagration; fused sulphur has no action, but sulphur vapour converts it into boron and phosphorus sulphides. Chlorine converts boron phosphide into boron trichloride and phosphorus pentachloride, with incandescence; bromine has no action in the cold, but combination takes place if the temperature is raised. Vapour of iodine, arsenic, or

phosphorus has no action at a dull-red heat. When heated at 500° in a current of nitrogen, boron phosphide yields no nitride, and, although at higher temperatures it loses phosphorus (as it does in a vacuum), no nitride is formed. When a mixture of boron phosphide and sodium is gently heated in a current of hydrogen, it rapidly becomes incandescent, with formation of sodium phosphide and boride. Potassium yields the same products at a lower temperature. A mixture of the boron phosphide with powdered magnesium becomes incandescent at about 500°, but aluminium has no action, except at a much higher temperature. Finely-divided silver, copper, and platinum react with the phosphide when gently heated, but mercury has no action at its boiling point. When boron phosphide is thrown into the strongest nitric acid, it takes fire, even in the vapour, and burns brilliantly on the surface of the liquid; on slightly heating, it dissolves immediately and completely. Concentrated solutions of hydrochloric and hydriodic acids have no action on the phosphide, and sulphuric acid has no action in the cold, but is reduced on heating. Concentrated hot solutions of potash and soda dissolve it slowly, whilst fused potash dissolves it completely with formation of hydrogen phosphide and potassium borate. Gaseous hydrogen fluoride attacks it below dull redness, with formation of boron fluoride, hydrogen, and phosphorus. Gaseous hydrogen chloride behaves similarly at a higher temperature. Boiling water has no action on the phosphide, but water vapour decomposes it at 400° with production of boric acid and hydrogen phosphide. Hydrogen sulphide at a dull-red heat yields boron sulphide and hydrogen phosphide. In ammonia at about 300° the phosphide burns, with formation of boron nitride and liberation of phosphorus.

Boron phosphide, B_5P_3, is obtained by heating the preceding compound at 1000° in a current of hydrogen. It has a paler colour than the phosphide PB, does not inflame in chlorine or nitric acid, and is not attacked by the latter, even when boiling. It is insoluble in all inorganic and organic solvents, burns with some difficulty in oxygen, and is attacked by fused nitrates with incandescence, but only with difficulty by metals and non-metals. It does not burn in chlorine below a dull-red heat.

If the hydrogen used for reduction contains water or oxygen, a white phosphoboric acid, also known as boron phosphate, is formed, and the same compound is obtained by the action of nitrogen oxides on a mixture of the phosphides. C. H. B.

Boron Phosphide. By A. Besson (*Compt. rend.*, **113**, 772—773). —The author draws attention to his previous note on the subject (Abstr., 1891, 1418), and describes an additional property of the phosphide. It is oxidised by dilute nitric acid to a substance, probably phosphoboric acid, which is left in nacreous plates on evaporating the solution to dryness, is soluble in water, and gives a white, gelatinous precipitate with excess of ammonia.

Moissan (*ibid.*, 787—788), commenting on this and the previous note, draws attention to the absence of numerical data justifying the formula BP attributed to the phosphide, and claims priority in the

systematic study of boron phosphides (*Compt. rend.*, **112**, 717, and **113**, 19). Jn. W.

The Influence of Steam and other Gases on the Combustion of Carbonic Oxide and Oxygen. By N. Békétoff (*Chem. Centr.*, 1891, ii, 449—450; from *Bull. Acad. St. Pétersbourg* [2], **2**, 175—179).—Having repeated Dixon's experiments (Trans., 1885, 94), the author has obtained the same results, namely, that a mixture of carbonic oxide and oxygen, when dried by means of phosphoric anhydride, is not exploded by the passage of an electric spark, and further, that if the gases be dried by sulphuric acid, which appears to leave a trace of moisture in the gas, the combustion proceeds so slowly that it may be followed with the eye. The presence of other gases, sulphurous anhydride, or nitrous oxide, had not a similar effect. Cyanogen, on the other hand, when present to the extent of 10 per cent., exerted an influence similar to that of steam, and caused an immediate explosion on the passage of the spark. Békétoff suggests that the action of cyanogen may be explained on the assumption that the heat liberated in the decomposition of the cyanogen is added to the heat of combustion of the carbon, and he further assumes that the dissociation temperature of the water molecule being lower than that of the oxygen molecule is the proper explanation of the fact that the presence of water in a mixture of carbonic oxide and oxygen assists the combustion of the latter gases. J. W. L.

Reactions of Carbonic Anhydride at High Pressures. By A. d'Arsonval (*Compt. rend. Soc. Biol.*, 1891, 320—321).—Liquefied carbonic anhydride is a powerful antiseptic. It does not coagulate albumin. At high pressures it can displace both organic and mineral acids. When urine is subjected to a pressure of 40 atmospheres of carbonic anhydride, crystals of uric acid are deposited. A dilute solution of potassium silicate similarly treated becomes solidified from the deposition of silicic acid. Carbonic anhydride at the same pressure is also able to liberate hydriodic and hydrobromic acids from solutions of potassium iodide and bromide respectively.

W. D. H.

Reduction of Cæsium. By N. Békétoff (*Chem. Centr.*, 1891, ii, 450—451; from *Bull. Acad. St. Pétersbourg* [2], **2**, 169—170).—The author has prepared considerable quantities of cæsium by reducing the hydroxide with aluminium. The reaction proceeds well, and is as readily carried out as the reduction of rubidium. The author refers to the results, which Winkler has recently published, on the heat of combination of the alkali metals, and points out that the deductions which Winkler has made are diametrically opposed to his own. The author finds that the combining heat of the alkali metals varies inversely with their atomic weights. He further urges that Winkler has not employed the oxides, but the hydroxides and carbonates, for his determinations, which are not suitable for the purpose.

J. W. L.

Properties of Cæsium and its Hydroxide. By N. Békétoff (*Chem. Centr.*, 1891, ii, 451; from *Bull. Acad. St. Pétersbourg* [2], **2**,

171—173).—The author has used a very pure specimen of cæsium sulphate as material on which to work. A determination of the sulphuric acid gave almost the theoretical amount, and by means of the spectroscope only a trace of rubidium could be detected.

The hydroxide was obtained from the sulphate by precipitation with barium hydroxide, and concentration of the filtrate in a silver dish, which was placed in a metal retort. In this manner carbonic anhydride was excluded. After concentration in the retort, the solution was transferred to a small silver dish, the remainder of the water evaporated, and the hydroxide finally fused. The silver dish was slightly attacked, and the silver oxide dissolved in the fused cæsium hydroxide; it was again precipitated, however, as the latter cooled. The quantity of silver oxide was inconsiderable. Cæsium hydroxide has a sp. gr. 4·0178, compared with water at 4°; the molecular volume = 37·3 (sodium hydroxide = 18; potassium hydroxide = 27; rubidium hydroxide = 32 ?). The molecular volume of the hydroxide corresponds with a very considerable diminution of volume during its formation from the elements. The heat of solution of the hydroxide in water is 15,876, which is higher than for all other alkali hydroxides. The heat of neutralisation of the hydroxide with hydrogen chloride (dilute) is 13,790, or nearly the same as that found by Thomsen for potassium hydroxide, or, indeed, for the other alkali hydroxides. Metallic cæsium was obtained by heating 114 grams of the hydroxide in a nickel retort with 27 grams of aluminium, and collecting the distilled metal in glass receivers; 20—25 grams of the metal were thus obtained.

The heat of combination of cæsium with water was found to be from 50 to 52 Cal. J. W. L.

Action of Sodammonium and Potassammonium on Metals. By Joannis (*Compt. rend.*, **113**, 795—798).—Sodammonium and potassammonium are decomposed by mercury, lead, and antimony, but are not affected by aluminium, silver, zinc, or copper. When a solution of sodammonium in liquefied ammonia is allowed to fall drop by drop on mercury, it is decomposed with the formation of a crystalline amalgam, Hg_8Na, which can be washed free from excess of the reagent with liquefied ammonia. Potassammonium under similar conditions yields an amalgam of the composition $Hg_{18}K$.

When pure lead is brought into contact with sodammonium, the reddish-brown liquid turns blue, and then green, and a little hydrogen is disengaged, owing to the spontaneous decomposition of the sodammonium. Finally, however, the metal is partially converted into an indigo-blue mass, which dissolves in liquefied ammonia to a bottle-green solution, and has the composition $Pb_4Na,2NH_3$. This substance decomposes at ordinary pressures, leaving a grey mass resembling spongy platinum, and oxidises rapidly on exposure to air, with evolution of heat. When thrown into water, the first portion dissolves completely, owing to the combination of the lead with the dissolved oxygen, and the subsequent solution of the oxide in the sodium hydroxide simultaneously formed, but as soon as the oxygen is used up, metallic lead is thrown down as a black, curdy precipitate.

Jn. W.

Influence of Ammonia on the Solubility of Ammonium Chloride. By R. Engel (*Bull. Soc. Chim.* [3], **6**, 17).—The presence of ammonia diminishes the solubility of ammonium chloride in water at 0° at first, but as the quantity of ammonia is increased, a corresponding increase in the chloride dissolved obtains. This result is probably due to the formation of compounds of ammonium chloride and hydroxide. Tables of values are given. T. G. N.

Precipitation of Copper by Iron and the Action of Iron on Ferric Solutions. By J. C. Essner (*Bull. Soc. Chim.* [3], **6**, 147—148).—In the wet method of copper extraction, very mixed qualities of scrap iron are employed. The reduced copper occurs in powder, grains, and filaments which cannot be readily washed free from the mud of ferric hydroxide formed. The author finds that the structure of the iron used exerts a marked influence on that of the copper obtained. By selecting the iron to be used, it is possible to obtain the reduced copper in a fibrous or granular condition, when it admits of being readily washed free from ferric hydroxide.

The occurrence of the mud of ferric hydroxide is due to the formation of a basic ferric sulphate, $Fe_2(OH)_4SO_4$. This salt is decomposed by iron as follows:—$6Fe_2(OH)_4SO_4 + Fe_2 = 6FeSO_4 + 4Fe_2(OH)_6$. On reduction with iron, dilute solutions of ferric sulphate give ferrous sulphate only.

The addition of a little sulphuric acid to the copper solution prevents the formation of the mud, and enables a clean deposit of copper to be obtained. W. T.

Mercurammonium Compounds. By E. Balestra (*Gazzetta*, **21**, ii, 294—305).—The author has examined some of the ammoniacal mercury compounds prepared by Millon (*Ann. Chim. Phys.* [3], **18**), and also described by Gmelin.

A. $NH_2HgCl,HgCl_2$.—This compound was obtained by Millon by adding small quantities of ammonia to a large excess of corrosive sublimate. The author succeeded in preparing a compound having the same physical and chemical characteristics by gradually adding to a solution of corrosive sublimate half the quantity of dilute ammonia required for the complete precipitation of the mercury. It does not evolve ammonia when boiled with potash, but a large quantity is given off on treating it with a cold concentrated solution of ammonium bromide, according to Pesci's reaction (Abstr., 1890, 1211), showing that the nitrogen is wholly contained in the mercurammonium radicle. Its composition was found to be $NHg_2Cl,2HCl$. When it is suspended in water and exactly neutralised with potash, it is converted into dimercurammonium chloride, NHg_2Cl.

B. $4NH_2HgCl,NH_2(Hg_2O)Cl$.—Millon obtained a yellow powder of the above composition by pouring a boiling solution of corrosive sublimate into a large excess of ammonia and thoroughly washing the product. Under these conditions, however, the author finds that a white precipitate is formed which loses ammonium chloride, on repeatedly washing with water, gradually acquiring a yellowish tinge; it then approximates in composition to dimercurammonium chloride.

The unaltered product has the composition of infusible white precipitate, NHg_2Cl,NH_4Cl.

C. $NH_2HgCl,2NH_2(Hg_2O)Cl_2$.—This compound was obtained by Millon in two ways: (1) by washing A completely with water, and (2) by adding small quantities of ammonia to a large excess of a boiling solution of corrosive sublimate. By washing A with water, the author, however, obtained a bright yellow powder of the composition $2NHg_2Cl,HgCl_2,H_2O$, which loses $\frac{1}{2}$ mol. H_2O at 105—110°.

By Millon's second method (the author added to a boiling 7 per cent. solution of corrosive sublimate half the quantity of ammonia required for neutralisation); a pale-yellow, amorphous powder was obtained having the composition NHg_2Cl,HCl. On neutralising this compound with potash, dimercurammonium chloride is formed. When it is washed with water, it is converted into the compound

$2NHg_2Cl,HgCl_2,H_2O$. S. B. A. A.

Solubility of Glass in Cold Water. By F. Kohlrausch (*Ber.*, **24**, 3560—3575).—The author has made experiments on the solubility of various kinds of glass by measuring the electrical conductivity of the solutions obtained on treating the glass with distilled water at 18°. He finds that the quantity of glass dissolved increases with the time, but not proportionately, the solvent action being more rapid at first; in the case of some of the best samples of glass, no appreciable action takes place even on prolonged contact. It was also found that of two solutions, prepared in like manner from two kinds of glass having approximately the same composition, the one may have almost twice the conductivity of the other; this result may be due to the two samples having undergone different treatment in their manufacture. The composition of the various kinds of glass employed and the numerical results of the experiments are given in tables.

The author also points out that the best and most rapid test for inorganic salts in distilled water is a measurement of its electrical conductivity; the presence of carbonic anhydride can be ascertained in the same way. F. S. K.

Reaction between Potassium Permanganate and Hydrogen Peroxide Solution. By R. Engel (*Bull. Soc. Chim.* [3], **6**, 17—19).—It often happens that when potassium permanganate solution is added to hydrogen peroxide solution, decolorisation does not at once ensue, but that when once the reaction has begun, decolorisation proceeds rapidly. Brodie attributed this result to the degree of dilution of the hydrogen peroxide, and Schöne to the action of light on this compound. The author regards neither of these hypotheses as tenable, and shows that the onset of the reaction is determined by the presence of a trace of a manganous salt in the mixed solutions; this results from the action of traces of sulphurous or nitrous compounds in the hydrogen peroxide solution on the permanganate; the manganous salt is then oxidised to manganic sulphate, which is unstable in presence of hydrogen peroxide. The addition

of a trace of manganous sulphate to the hydrogeu peroxide solution before running in the permanganate solution determines decolorisation at the onset. T. G. N.

Action of Ferric Chloride on Metallic Sulphides. By Cammerer (*Chem. Centr.*, 1891, ii, 525; from *Berg. Hütten Zeit.*, **50**, 295—298).—(For the first part of this work, see this vol., p. 18.) Ferric chloride reacts with stannic sulphide forming stannic chloride, sulphur, and ferrous chloride. Mercuric sulphide is converted into mercuric chloride, sulphur and ferrous chloride being formed at the same time. The mercuric chloride at first formed reacts again with two more molecules of mercuric sulphide, with production of Heumann's double salt, $2HgS,HgCl_2$. This is a white substance, which is blackened by alkalis, but appears to be regenerated by the subsequent action of nitric acid.

With silver sulphide, ferric chloride reacts, forming silver chloride, sulphur, and ferrous chloride. With the sulphides of lead, bismuth, cobalt, and manganese, ferric chloride reacts, the corresponding chloride of the metal is formed together with ferrous chloride, and the sulphur is set free. Most of the reactions take place readily and completely. J. W. L.

Coloration of Solutions of Cobalt and the State of the Salts in the Solutions. By A. Étard (*Compt. rend.*, **113**, 699—701).—Cobalt iodide yields red, green, and blue solutions. Its solubility at various temperatures is as follows:—

t	−22°	−8°	−2°	+9°	14°	25°	34°	46°
Sol...	52·4	56·7	58·7	61·4	61·6	66·4	73·0	79·0

t	60°	82°	111°	156°
Sol...	79·2	80·7	80·9	83·1

Cobalt chloride yields rose-coloured or blue solutions, and its solubilities are as follows:—

t	−22°	−4°	+7°	11°	12°	25°	34°	41°
Sol...	24·7	28·0	31·2	31·3	32·5	34·4	37·5	39·8

t	45°	49°	56°	78°	94°	96°	112°
Sol...	41·7	46·7	48·4	48·8	50·5	51·2	52·3

The garnet-red, hexahydrated cobalt iodide yields a dull red solution between −22° and about +20°, the solubility between these limits being represented by a right line. Above 20°, the liquid becomes brown, then olive, and finally at 35° deep chrome-green, this colour persisting even up to 320°. The deep green liquid yields green, lamellar crystals of the composition $CoI_2,4H_2O$. The formation of this salt begins at 20°, and since it is more soluble than the red salt, and the two solubilities are superposed, there is a gradual increase in the total solubility between 20° and 35°, the curve being convex towards the axis of temperature. Above 35°, the green salt alone exists in solution, and its solubility is represented by a right

line. If it were possible to make experiments above 320°, it is probable that the green liquid would become blue, and would contain a lower hydrate analogous to $CoCl_2,2H_2O$. Such a blue solution is obtained when a solution of the cobalt iodide is poured into a saturated solution of magnesium chloride.

In the case of cobalt chloride, the hydrate, $CoCl_2 + 6H_2O$, dissolves without change between −22° and +25°, the solution has a pure rose colour, and the solubility is represented by a right line. At 25°, dissociation begins, and the more soluble blue hydrate, $CoCl_2 + 2H_2O$, is formed, the colour of the solution changing to purple, and finally, at 50°, to blue, this colour persisting up to 300°. Between 25° and 50°, the curve of solubility is convex towards the axis of temperature, but beyond 50°, it again becomes a right line.

The changes of colour are not due to the presence of free acid or an acid salt, for they can be observed in presence of calcium carbonate or precipitated cobalt carbonate. C. H. B.

Oxidation of Nickel Carbonyl. By Berthelot (*Compt. rend.*, **113**, 679—680).—Nickel carbonyl can be kept under water in a flask without undergoing any alteration, provided that air is excluded, but in presence of air, green nickelous hydroxide, free from carbon, separates, and, at the same time, some of the nickel carbonyl escapes into the air and is oxidised to a white powder which, in mass, has a pale greenish tinge. It has the composition C, 5·3; NiO, 53·3; H_2O, 40·1 = 98·7, whilst the formula $C_2O_3Ni_3,10H_2O$ requires C, 5·6; NiO, 52·5; H_2O, 41·9 = 100. The compound would, therefore, seem to be the oxide of a complex radicle, analogous to croconic and rhodizonic acids. It is possible that one part of the nickel may be present in the form of nickel monoxide, mixed or combined with a complex oxide of the simpler formula C_2ONi, belonging to the ethylene type or to a more condensed type of the same order, this oxide being formed thus, $C_4O_4Ni + O = C_2ONi + 2CO_2$. C. H. B.

Action of Hydrogen Phosphide on an Ethereal Solution of Bismuth Tribromide. By A. Cavazzi and D. Tivoli (*Gazetta*, **21**, ii, 306—308).—When a solution of bismuth tribromide in dry ether is allowed to fall gradually into a vessel containing dry hydrogen phosphide, a lustrous, black substance is formed which strongly adheres to the sides of the vessel. It becomes dull and hard on drying in a vacuum, and probably has the composition $PBrH(BiBr_2)_3$, being formed according to the equation $3BiBr_3 + PH_3 = 2HBr + PBrH(BiBr_2)_3$. It is very hygroscopic, and is gradually decomposed by cold water and rapidly by boiling water, hydrogen phosphide, hydrobromic and phosphoric acids being formed and bismuth liberated. On heating it with a solution of potash, potassium bromide and phosphate are formed with evolution of hydrogen and hydrogen phosphide.

Concentrated sulphuric acid has no action on it at the ordinary temperature, but, on boiling, bismuth sulphate, phosphoric acid, hydrobromic acid, bromine, and sulphurous anhydride are formed. Concentrated nitric acid also acts very violently on it. When triturated

with fragments of sodium amalgam, it ignites and decomposes with more or less violence, according to the richness of the amalgam in sodium. When heated at 220° in an atmosphere of dry carbonic anhydride, it has the same composition as when dried in a vacuum. When heated in the air, it becomes viscid and decomposes with some violence and with evolution of fumes of bromine, bismuth bromide, and phosphoric anhydride. S. B. A. A.

Auric Sulphide. By U. Antony and A. Lucchesi (*Gazzetta*, **21**, ii, 209—212).—Auric sulphide, prepared by the authors' method (Abstr., 1891, 526), is a graphitic, amorphous powder having a sp. gr. of 8·754 compared with water at 0°; it decomposes into its elements at 197—200°.

Hydrochloric acid has no action on auric sulphide, concentrated nitric acid oxidises it in the cold with separation of gold, whilst aqua regia readily dissolves it. Caustic alkalis (15 per cent.) decompose the sulphide on heating, metallic gold and alkali sulphide and thiosulphate being obtained. Ammonia solution, on prolonged contact, decomposes it, yielding sulphuric acid, free sulphur, and a little hydrogen sulphide. The action of potassium cyanide solution on auric sulphide differs from its action on aurous sulphide and aurosoauric sulphide, both of which dissolve and are reprecipitated by acids. Auric sulphide dissolves in aqueous potassium cyanide (25 per cent.) to a yellow solution, which, on boiling, becomes colourless and deposits aurous potassium cyanide on cooling, $Au_2S_3 + 6KCN = 2AuKC_2N_2 + K_2S + 2KCNS$. This reaction shows the substance to be homogeneous, the auric sulphide prepared by Berzelius having been shown by Krüss and Hoffmann (Abstr., 1887, 1019; 1888, 28) to be a mixture of aurosoauric sulphide with sulphur.

Hydrosulphide and polysulphides of ammonia dissolve auric sulphide readily on warming, gold being deposited. The sulphides and polysulphides of the alkali metals dissolve the substance slowly; whilst the alkali hydrosulphides dissolve it in the cold, yielding a deep reddish-brown solution, which, on boiling, becomes pale yellow and deposits gold. These solutions, on treatment with hydrochloric acid, give a flocculent, yellow precipitate, probably consisting of auric hydrosulphide, which soon turns brown with formation of hydrogen sulphide and auric sulphide.

On precipitation with alcohol at −10°, a concentrated solution of auric sulphide in sodium hydrosulphide gives a yellowish precipitate; this, when filtered through asbestos at the same temperature in an atmosphere of nitrogen and washed with alcohol, yields a white, crystalline product which soon darkens in colour. The freshly prepared substance is very soluble in water and is probably sodium sulphaurate, but it decomposes so rapidly that trustworthy analyses could not be made. W. J. P.

Iodonitro- and Bromonitro-platinum Compounds. By M. Vézes (*Compt. rend.*, **113**, 696—698).—The relative stability of the nitro- and haloïd groups in the iodonitro-platinum compounds is the inverse of that observed in the case of the chloronitro- and bromo-

nitro-compounds (Abstr., 1891, 807). The iodine is displaced by nitrogen oxides, and the stable term of the series is the platonitrite and not the platoiodide. Nitrogen oxides readily decompose potassium platoiodide with liberation of iodine; whilst, on the other hand, iodine in the form of vapour or in solution in hydriodic acid or a solution of potassium iodide does not decompose potassium platonitrite.

The action of an alcoholic solution of iodine on a warm solution of potassium platonitrite, however, yields large, brilliant prisms of the compound $Pt,2NO_2,K_2I_2 + 2H_2O$, described by Nilson, but this, although stable in warm solutions, is decomposed by nitrogen oxides or potassium nitrite, with liberation of iodine and formation of the platonitrite. The author has so far failed to obtain a compound $Pt,4NO_2,K_2I_2$, analogous to the platichloronitrite and the platibromonitrite previously described.

If, however, an excess of an alcoholic solution of iodine is added to a warm concentrated solution of the platonitrite, and the mixture is concentrated as rapidly as possible at a gentle heat, *potassium nitroso-plati-iodide*, PtI_3,NO,K_2I_2, separates on cooling in small, brilliant, black crystals, which remain unaltered at 100°. When heated in a current of hydrogen, this compound yields water, ammonium iodide, iodine, hydrogen iodide, and a residue of potassium iodide and platinum.

If the liquid is slowly concentrated (without ebullition) a different compound is obtained on cooling. It is *potassium platitetraiodonitrite*, $PtI_4,2NO_2,K_2$, and separates in small, well-defined, black crystals with a greenish lustre. Like the preceding compound, it is only slightly soluble in water, yielding a deep brown solution, and it undergoes no change at 100°. When heated in a current of hydrogen, it yields water, ammonium iodide, iodine, and hydrogen iodide, with a residue of potassium iodide and platinum.

When the mixture yielding these two salts is submitted to prolonged ebullition, the excess of iodine is expelled and potassium platoiodonitrite is formed.

When bromine-water is added to a solution of potassium platoiodonitrite until all the iodine is expelled, the brown liquid, when concentrated in a dry vacuum, yields yellow, tabular crystals. The same crystals are obtained by heating a solution of potassium platibromonitrite, $Pt,4NO_2,K_2Br_2$, with alcohol at 80°, aldehyde and other gases being evolved. This new compound is *potassium platobromonitrite*, $Pt,2NO_2,K_2Br_2 + H_2O$, and is very soluble in water. At 100°, it becomes anhydrous and bright yellow; at a higher temperature, it blackens with evolution of nitrogen oxides, a residue containing potassium bromide and platinum in the proportions Pt + 2KBr being left. When heated in hydrogen, it yields the same residue without any formation of ammonium bromide, bromine, or hydrogen bromide.

C. H. B.

Two New Seleno-salts. By R. Schneider (*J. pr. Chem.* [2], **44**, 507—512).—*Potassium platinoselenostannate*, $K_2Pt_3SnSe_6$, is prepared by melting together 10 parts of platinum sponge, 6—8 parts of tin selenide, 30—40 parts of potassium carbonate, and 30—40 parts of selenium in a covered porcelain crucible so that the mass shall remain liquid for 8—10 minutes after the frothing has ceased. The melt is extracted

with water, and the undissolved residue digested with concentrated potassium hydroxide solution, whereby the selenostannate is left unattacked. It forms small, well-defined, hexagonal tables which are leaden-grey by reflected light and have a strong metallic lustre; in thin layers they are reddish-brown by transmitted light. In its general habitus it is very similar to the author's potassium platinosulphostannate (*Ann. Phys. Chem.*, **138**, 612). At the ordinary temperature, it is stable in air; when heated in air, it loses all its selenium, the residue consisting of a mixture of platinum with potassium stannate. It is not attacked by water, ammonia, potash, or hydrochloric acid, either hot or cold.

Sodium platinoselenostannate, $Na_2Pt_3SnSe_6$, cannot be obtained by merely substituting sodium carbonate for potassium carbonate in the above prescription. It is readily formed, however, when 10 parts of platinum sponge, 5—6 parts of tin selenide, 40 parts of potassium carbonate, 5—6 parts of sodium carbonate, and 40 parts of selenium are fused together, and the melt treated as described above. It forms leaden-grey, microscopical, hexagonal laminæ with a brilliant, metallic lustre; the remarks concerning the potassium salt apply also to this.

A. G. B.

Saline Compounds of the Lower Ruthenium Oxides with the Higher Oxides. By A. Joly (*Compt. rend.*, **113**, 694—695.)—When the products of the sudden decomposition of potassium perruthenate at 440° are kept for a long time at this temperature, interaction takes place with formation of a black, crystalline compound of the composition $K_2O,6Ru_2O_5$. Sodium perruthenate at 440° loses oxygen and water, and after treatment of the residue with water, which removes sodium oxide and the orange sodium ruthenate, a black crystalline powder is left with a composition approximating very closely to that for $Na_2O,3Ru_2O_5$. Barium ruthenate, $BaRuO_4$, at 440° loses oxygen, and yields a ruthenite, $BaRuO_3$, different in properties from a mixture of barium monoxide and ruthenium dioxide. The author directs attention to the analogy between these compounds and the products obtained by Rousseau from the permanganates, and the product K_2O,Os_2O_5, obtained by himself from potassium osmiamate.

C. H. B.

Action of Light on Ruthenium Peroxide. By A. Joly (*Compt. rend.*, **113**, 693—694).—When sealed tubes containing perfectly dry ruthenium peroxide are kept in the dark, no alteration takes place, but on exposure to sunlight, the walls of the tube become coated with a pale brown layer, which gradually increases in thickness and eventually transmits only red light. Beyond this point, the peroxide behind undergoes no further change. The brown deposit dissolves at once in potassium hydroxide solution, forming a yellow liquid without any trace of green, and in hydrochloric acid with evolution of chlorine and formation of a solution of ruthenium sesquichloride. It seems, therefore, that when exposed to sunlight, ruthenium peroxide is reduced to the trioxide, RuO_3. C. H. B.

Mineralogical Chemistry.

Sulphur, Orpiment, and Realgar in the Yellowstone National Park. By W. H. Weed and L. V. Pirsson (*Amer. J. Sci.*, **42**, 401—405).—In the Yellowstone National Park there are, besides the geyser basins, many small hot-spring areas where fumeroles and solfataras are still active. At most of these places, deposits of sulphur occur in and around the vents from which the vapours issue. At Highland Hot Springs and at Crater Hill the vents are very abundant, and large deposits of sulphur are found, frequently forming clusters of delicate crystals. Details of the measurement of the crystals are given by the authors. Although no analysis was made, the material is apparently of great purity.

The presence of arsenic in the hot-spring waters of the Yellowstone Park was noticed by A. Hague (Abstr., 1888, 122), and a careful search for deposits of arsenical sulphides was rewarded by the discovery of realgar and orpiment at the Norris Geyser basin. Siliceous sinter is the only other mineral occurring with these arsenical sulphides. B. H. B.

Occurrence of a Natural Gold Sulphide. By T. W. T. Atherton (*Chem. News*, **64**, 278).—The author observed the occurrence of gold in an exceptionally fine state of sub-division in an arsenical pyrites; further investigation showed that this gold could be extracted by heating the finely pulverised pyrites for some hours with a solution of sodium sulphide. It hence appears that the gold, or at least some of it, is present as sulphide. The following is the percentage composition of the ore in general; it also runs 5 ozs. 3 dwts. 8 grs. of gold, and 16 dwts. of silver, to the ton.

SiO_2.	Al_2O_3.	CaO.	S.	As.	Fe.	Co.	Ni.
13·94	6·59	0·9	16·58	33·27	27·72	0·96	trace

It is found in a large irregular lode of arsenical pyrites in a felsite dyke in a mica-schist country. Both in the lode and in its vicinity there are large quantities of pyrophyllite. D. A. L.

New Analyses of Uraninite. By W. F. Hillebrand (*Amer. J. Sci.*, **42**, 390—393).—The author gives the following analyses of uraninite. (See next page.)

I*a* is a re-analysis of nivenite from Llano Co. Texas. It agrees in the main with the original analysis by Hidden and Mackintosh, I*b* (Abstr., 1890, 457). II is from a new locality, Marietta, Grenville Co., South Carolina. III is from the Villeneuve mica mine, Ottawa Co., Quebec. IV represents the composition of a specimen from Johanngeorgenstadt, in Saxony. None of these specimens was fresh, and consequently no light could be thrown on the ultimate composition of the mineral. Valuable data, however, are afforded as to the

presence or absence of nitrogen (compare Abstr., 1890, 456; 1891, 527), and of the rare earths. The species, it will be seen, may be broadly divided into two groups, one of which is characterised by the presence of rare earths, and the other by their absence. With the former group, nitrogen appears to be invariably associated. Probably all the varieties of the first group occur in crystals, whilst the members of the second group are generally free from crystalline form.

	UO_3.	UO_2.	ThO_2.	ZrO_2.	CeO_2.	La group.	Y group.	CaO.
I*a*.	44·17	20·89	6·69	0·34	0·34	2·36	9·46	0·32
I*b*.	46·75	19·89	7·57	—	—	—	11·22	—
II.	83·95		1·65	0·20	0·19	2·05	6·16	0·41
III.	41·06	34·67	6·41	?	0·40	1·11	2·57	0·39
IV.	59·30	22·33	none					1·00

	PbO.	H_2O.	N.	SiO_2.	Insol.	Fe_2O_3.
I*a*.	10·08	1·48	0·54	0·46	1·47	0·14
I*b*.	10·16	2·54	—	—	1·22	0·58
II.	3·58	—	—	—	0·20	trace
III.	11·27	1·47	0·86	0·19	0·13	0·10
IV.	6·39	3·17	0·02	0·50	—	0·21

B. H. B.

Discovery of Diamonds in Meteoric Iron. By A. E. Foote (*Amer. J. Sci.*, **42**, 413—417).—In 1891, a meteorite was found near Cañon Diablo in Arizona, and was thought to form part of a vein of metallic iron. The largest mass discovered weighs 201 lbs., and has a somewhat flattened rectangular shape showing deep pits, three of which pass entirely through the iron. One other large mass was found weighing 154 lbs. A mass weighing 40 lbs. was broken in pieces with a trip hammer, and it was in cutting one of the fragments of this mass that diamonds were discovered. The diamonds are black and white, their nature being established by their hardness and indifference to chemical agents. Carbon in the form of a pulverulent iron carbide occurs in the same cavity with the diamonds. The proportion of nickel in the general mass is 3 per cent. B. H. B.

The Tonganoxie Meteorite. By E. H. S. Bailey (*Amer. J. Sci.*, **42**, 385—387).—This meteorite was found in 1886 near Tonganoxie, Leavenworth Co., Kansas. The specimen originally weighed 26 lbs. Its shape is that of an irregular triangular pyramid, $9\frac{1}{2}$ inches long, $6\frac{1}{2}$ inches wide, and $4\frac{1}{2}$ inches deep. The sp. gr. is 7·45. As shown by a photograph accompanying the author's paper, the surface of the meteorite is covered with numerous depressions. The entire exterior is covered with a reddish-black coating of iron oxide, with occasional drops of chloride of iron exuding after having been exposed to the air. The analysis of the meteorite gave the following results:—

Fe.	Ni.	Co.	P.	Cu.	Total.
91·18	7·93	0·39	0·10	trace	99·60

On treatment with nitric acid, the surface exhibited the Widman stättian figures very clearly. B. H. B.

Composition of some Subterranean Waters from near Port-Vendres. By J. C. Essner (*Bull. Soc. Chim.* [3], **6**, 148—151).—Eleven samples of water collected from the valley of Cosperons, on the Mediterranean slope of the Albères, in the commune of Port-Vendres, were found to contain calcium, magnesium, aluminium, chlorine, and sulphuric acid. One sample only was neutral, seven contained from 0·024 to 0·065 gram of free sulphuric acid per litre, and three contained respectively 0·175, 0·285, and 0·506 gram of free acid per litre.

The neighbouring rocks contain iron pyrites disseminated throughout; the fissures are filled with a yellow powder consisting of ferric oxide, together with some basic ferric sulphates. The natural acidity of these waters is attributed to the formation of this deposit. The waters retain only a trace of iron, as the dissolved salts decompose with formation of free sulphuric acid. This view is confirmed by the behaviour of rain-water collected in a cistern at a height of 250 metres above the level of the sea after several months of dry weather. The cistern and works were constructed of stones and débris of the surrounding rocks. Water taken from the cistern, dirty as collected, gave 9·073 grams of dissolved crystallised substances, and 0·105 gram of suspended matter; it was slightly acid. After six days rest, the filtered water already yielded only 6·179 grams of crystallised residue per litre, and 2·997 grams of basic ferric sulphate had been deposited. After an exposure to free air of one month, the water, after filtration, contained only traces of iron, together with 0·765 gram of sulphuric acid (H_2SO_4), and gave 1·010 grams of residue calcined at a red heat, containing calcium, magnesium, and aluminium, with traces of chlorine, sulphuric acid, iron, potassium, and sodium.

The analysis of the primitive water gave:—

Iron calculated as Fe_2O_3	1·500	grams per litre.
CaO	0·637	,,
MgO	0·354	,,
Al_2O_3	0·012	,,
Chlorine	0·024	,,
Total H_2SO_4	3·672	,,

W. T.

Organic Chemistry.

A Method for Determining the Constitution of Saturated and Unsaturated Halogen Derivatives and Hydrocarbons. By M. Wildermann (*J. pr. Chem.* [2], **44**, 470—492).—This is a method for the determination of the constitution of the higher

members (above $n = 4$) of the aliphatic series, founded on alternate halogenisation and removal of the elements of halogen hydro-acids, with determination of the heats of combustion of the various hydrocarbons produced. The paper is not suitable for abstraction, as the method could not be made intelligible without a full reproduction of the details both of the argument employed and of the various examples given. A. G. B.

Platinum Thiocyanate and Platinothiocyanates. By I. Guareschi (*Chem. Centr.*, 1891, ii, 620—622; from *Giorn. R. Acad. Med.*, 1891).—The author has prepared potassium platinothiocyanate according to the methods of Buckton, Wyrouboff and Norton. He finds that the salt crystallised from alcohol is anhydrous, whilst that crystallised from water contains 2 mols H_2O. This it loses if dried over calcium chloride, but he does not find that it is so readily lost on exposure to the air at ordinary temperatures as Wyrouboff stated.

Potassium platinothiocyanate, $K_2Pt(CNS)_6$, gives characteristic precipitates with many organic bases, and may be used as a test for certain alkaloïds. The platinothiocyanates of the tertiary amines are less soluble than the corresponding salts of the secondary and primary amines. In many cases, the double salts of the secondary bases melt at a lower temperature than those of the primary.

Monomethylamine platinothiocyanate, $(NH_2Me)_2,H_2Pt(CNS)_6$, is prepared by allowing the mixed solutions of potassium platinothiocyanate and of methylamine hydrochloride to remain for several days, when the double thiocyanate crystallises out in long, red, rhombic prisms. The *dimethylamine* salt, $(NHMe_2)_2,H_2Pt(CNS)_6$, is precipitated as red prisms or needles on mixing the not very concentrated solutions of the respective salts. It melts at 160—170° with decomposition, and is soluble in cold water, more readily in hot water, readily soluble in alcohol, insoluble in ether. The *trimethylamine* salt, $(NMe_3)_2,H_2Pt(CNS)_6$, forms red prisms, sparingly soluble in cold water, soluble in alcohol, but insoluble in ether; it melts at 175° with decomposition.

The *ethylamine* salt is similar to the methylamine salt. The *diethylamine* salt, $(NHEt_2)_2H_2Pt(CNS)_6 + 2H_2O$, is prepared by mixing 1 part of the hydrochloride in 6 parts of water with potassium platinothiocyanate. A liquid precipitate at first separates which rapidly solidifies to a mass of short prisms, or rectangular, lemon-yellow plates, which, after drying in the air, melt at 58—58·5°, and in the anhydrous condition, melt at 79—80°. It is sparingly soluble in cold water, more readily in hot water, very soluble in alcohol, insoluble in ether. The *triethylamine* salt, $(NEt_3)_2,H_2Pt(CNS)_6$, is precipitated, when the solution of the hydrochloride, acidified with hydrochloric acid, is added to potassium platinothiocyanate, as a thick, red liquid, which solidifies gradually when agitated. When recrystallised from water, it separates in the same way. It consists of golden-yellow plates, melts at 165—167°, and decomposes at 180°. It is sparingly soluble in cold water, more readily in hot water and in alcohol, insoluble in ether.

Propylamine, butylamine, and amylamine react in the same manner as methylamine and ethylamine.

The *ethylenediamine* salt, $C_2H_4N_2H_4,H_2Pt(CNS)_6$, is a yellow precipitate, sparingly soluble in water, and blackens at 140—150°. The *pentamethylenediamine* salt, $C_5H_{14}N_2,H_2Pt(CNS)_6$, is obtained by precipitating the solution of the hydrochloride with platinum thiocyanate. The precipitate soon becomes crystalline, and forms reddish needles which commence to turn brown at 160°, and become quite black at 176°, but do not melt. It is soluble in alcohol and water, but insoluble in ether.

The *diacetoneamine* salt, $(COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2)_2,H_2Pt(CNS)_6$, is obtained by precipitating the solution of diacetoneamine oxalate with the platinothiocyanate. It is thus obtained as a crystalline precipitate, which, when recrystallised from hot water, forms red prisms, soluble in alcohol, insoluble in ether. It melts at 165° with decomposition. The *guanidine* salt, $(C_6H_5N_3)_2,H_2Pt(CNS)_6$, is obtained in beautiful red crystals on mixing solutions of guanidine hydrochloride with the platinothiocyanate. It is also obtained when the solution of guanidine thiocyanate is mixed with platinum chloride. It blackens at 170—175° without melting.

The *aniline* salt, $(NH_2Ph)_2,H_2Pt(CNS)_6$, forms dark-red crystals which melt at 100—105°, soluble in alcohol and water, insoluble in ether. The *α-naphthylamine* salt forms a dark-yellow precipitate, the *β*-salt a light-yellow precipitate, from solutions of the hydrochlorides; they are both somewhat difficult to obtain crystalline; they decompose readily on exposure to moist air, especially the *α*-salt. They both melt to brown liquids, the *α*-salt at 140°, the *β*-salt at 120°

Paratoluidine, allylamine, and furfurine are precipitated in like manner.

Phenylhydrazine reduces the solution of the platinothiocyanate. Tetrahydro-*β*-naphthylamine forms a yellow, crystalline precipitate. The *pyridine* salt, $(C_5H_5N)_2,H_2Pt(CNS)_6$, crystallises in red prisms, and is precipitated from the solution of the hydrochloride. It is not changed by exposure to the air, but commences to decompose at 100—105° and melts at 170—172° to a black liquid; it is soluble in hot water, but only sparingly in cold water. Protracted boiling with water causes decomposition. The *piperidine* salt, $(C_5H_{11}N)_2,H_2Pt(CNS)_6$, is precipitated at first as a liquid, which later solidifies in lemon-yellow prisms, sparingly soluble in cold water, readily so in hot water and in alcohol. *Coniine* as hydrochloride or as hydrobromide is precipitated, if the solution be not too dilute, as a red oil, which could not be obtained crystalline. A solution of coniine hydrobromide 1 : 1000 is not precipitated, but *nicotine* is precipitated as yellow crystals at a dilution of 1 : 3000. This salt is almost insoluble in cold water, and may serve to distinguish coniine from nicotine. The *sparteïne* salt forms a sulphur-yellow, powdery precipitate. The *α- and β-quinoline* salts are precipitated as yellow, microscopical crystals; the *α*-salt is the darker; even a solution of 1 : 6000 is precipitated.

Ephedrine, *apomorphine*, *apocodeïne*, *cocaïne*, and *ecgonine* are likewise precipitated. *Glycosamine* is not precipitated.

The reaction was examined in the case of the following alkaloïds with the view of determining the delicacy in each case. *Strychnine* solution, 1 : 40,000, gave a crystalline precipitate after some time; *brucine*, 1 : 18,000; *atropine*, 1 : 20,000; *morphine*, 1 : 1000; *veratrine*, 1 : 10,000; *nicotine*, 1 : 3000; *codeïne*, 1 : 2000, all precipitate immediately. *Quinine*, *cinchonine*, *quinidine*, *cinchonidine*, 1 : 100,000, also give precipitates immediately; *aspidospermine*, 1 : 40,000 is also precipitated immediately. J. W. L.

Decomposition of Hydrocarbons with Steam. By Coquillion and Henrivaux (*Chem. Centr.*, 1891, ii, 577; from *J. Usines à Gaz*, 1890, 355).—The authors have determined the composition of the gaseous mixture obtained by heating methane and steam together. When the gases were subjected to the action of an incandescent platinum wire fixed at the lower end of the eudiometer, the gas produced had the composition: 2·45—2·50 per cent. CO_2, 13·68—16·50 per cent. CO, 17·84—14·60 per cent. CH_4; 66·03—66·40 per cent. H. When the methane and steam were passed through three iron tubes heated to redness, the resulting gas had the composition: 1·00 per cent. CO_2, 19·86 per cent. CO, 8·24 per cent. CH_4, 70·90 per cent. H. After passing through tubes heated to a white heat, the resulting gas has the composition: 12·01 per cent. CO_2, 7·35 per cent. CO, 50·64 per cent. H, no methane remaining. J. W. L.

Hydrocarbons from α- and β-Amyrin. By A. Vesterberg (*Ber.*, **24**, 3834—3836).—As already stated (Abstr., 1887, 733; 1891, 165), α- and β-amyrin are converted by phosphorus pentachloride into dextro-α- and β-amyrilene, $C_{30}H_{48}$, and α-amyrin by phosphorus pentoxide into lævo-α-amyrilene, $C_{30}H_{48}$. Dextro-α-amyrilene is sparingly soluble in acetic acid, readily in light petroleum and benzene, and commences to decompose at its boiling point. Lævo-α-amyrilene is prepared by adding a benzene solution of α-amyrin to phosphorus pentoxide, allowing the cherry-red jelly to remain for some days, and adding water to remove phosphoric acid. The benzene solution, on spontaneous evaporation, deposits prismatic crystals surrounded by a glutinous mass; the latter is removed by ether, and the residue recrystallised from hot benzene. It forms rhombic crystals ($a : b : c = 0·789 : 1 : 0·505$), melts at 193—194°, is sparingly soluble in ether, more readily in light petroleum and benzene, and has the sp. rotatory power $[\alpha]_D = -104·9$.

β-Amyrilene is almost insoluble in alcohol and acetic acid, and less readily soluble in ether, light petroleum, and benzene than dextro-α-amyrilene. H. G. C.

Derivatives of Glycerol. By E. Seelig (*Ber.*, **24**, 3466—3471).—Diacetylglycerol (diacetin) is obtained in quantitative yield by boiling 95 per cent. glycerol (400 grams) with glacial acetic acid (1000 grams) in a reflux apparatus for 8½ hours, distilling up to 116°, replacing the distillate (about 270 grams) by an equal weight of fresh glacial acetic acid, boiling for a further 17 hours, and, after distilling off the acetic acid, rectifying the product under a pressure of

40 mm. It boils at 172—174° (40 mm.), and at 259—261° (760 mm.) has a sp. gr. 1·178, is miscible with water, ether, chloroform, and benzene, but almost insoluble in light petroleum and carbon bisulphide. On one occasion the author treated a sample of ordinary glycerol in the above manner, and obtained a product which was only miscible with water to a limited extent, and did not become acid on boiling with it. Diacetylglycerol can only be converted into the triacetyl derivative (triacetin) as follows:—Coarsely pulverised, anhydrous sodium acetate (60 grams) is well mixed with acetic anhydride (150 grams), diacetylglycerol (200 grams) added, and the mixture boiled in a reflux apparatus for 16 hours; the product is shaken with $1\frac{1}{2}$ times its volume of ether and an equal quantity of water. when the triacetyl derivative is dissolved by the ether, and is isolated by distillation. It boils at 171° (40 mm.), and at 258—259° (760 mm.), has a sp. gr. 1·155, is sparingly soluble in water, and, unlike the diacetyl compound, is not decomposed when boiled with it; it is miscible with alcohol, ether, chloroform, and benzene, but almost insoluble in light petroleum and carbon bisulphide. It would thus appear that the triacetylglycerol described by Schmidt (Abstr., 1880, 312) was in reality the diacetyl derivative, and since a mixture of the two cannot be separated from one another, Böttinger's method (Abstr., 1891, 1183) is invalid.

When diacetylglycerol is dissolved in glacial acetic acid, saturated with hydrogen chloride, and, after heating at 100° for two hours, distilled under a pressure of 40 mm., two fractions, consisting of impure dichloracetyl derivatives, pass over at 101—107° and at 107—113° respectively, whilst chlorodiacetylglycerol, contaminated apparently with chloracetylglycerol, passes over at 137—144° (see below), and, lastly, unaltered diacetylglycerol distils; lower boiling compounds are also formed. The same result is obtained by leading a stream of hydrogen chloride through boiling diacetylglycerol. When cooled acetic anhydride (130 grams) is saturated with dry hydrogen chloride, mixed with diacetylglycerol (190 grams), again saturated with hydrogen chloride, 70 grams of the gas being absorbed in all, and the mixture heated at 110° for 30—40 hours, a chlorodiacetylglycerol boiling at 142—149° (40 mm.), or at 230—240° (760 mm.), a dichloracetylglycerol boiling at 108—112° (40 mm.), or at 189—199° (760 mm.), together with much triacetylglycerol and lower boiling compounds, are obtained; whilst if hydrogen chloride is passed through boiling triacetylglycerol for 70 hours, a chlorodiacetylglycerol boiling at the same temperature as the last-mentioned one, and having a sp. gr. 1·204, is produced. When the fraction boiling at 137—144° (40 mm.) from diacetylglycerol and hydrogen chloride is heated with an excess of acetic anhydride at 180—190°, a chlorodiacetylglycerol boiling at 141—148° (40 mm.) is obtained, whilst a similar compound is produced by heating α-chlorhydrin with an excess of acetic anhydride. When dichlorhydrin (prepared from α-chlorhydrin) is heated with acetic anhydride, it yields two dichloracetylglycerols boiling at 108—112° and at 112—116° (40 mm.) respectively. The dichloracetylglycerol boiling at the lower temperature is probably the symmetrical derivative, and, since only one

monochloro-derivative is formed from the diacetylglycerol, the two acetoxy-groups in this compound probably occupy consecutive positions, and support is afforded to this view by the fact that the diacetylglycerol yields an aldehyde on oxidation with nitric acid; the *hydrazone* from the latter melts at 161°. A. R. L.

Reactions of Xylose and Arabinose. By Tollens (*Bull. Soc. Chim.* [3], **6**, 161—162).—This is a note containing extracts from memoirs by Wheeler and Tollens (*Annalen*, **254**, 314), and by Allen and Tollens (*Annalen*, **260**, 304), which show that the coloured reactions of xylose with orcinol and phloroglucinol, given by Bertrand in the *Bull. Soc. Chim.* [3], **5**, 932, were already known.

W. T.

Oxidation Products of α- and β-Amyrin. By A. Vesterberg (*Ber.*, **24**, 3836—3843).—Both α- and β-amyrin, when oxidised with chromic acid in acetic acid solution, yield as chief products the corresponding ketones (or, possibly, aldehydes), α- and β-amyrone.

α-Amyrone, $C_{30}H_{48}O + H_2O$, crystallises from a mixture of alcohol and acetic acid in large tablets, melts at 125—130°, dissolves readily in ether, hot benzene, and acetic acid, sparingly in light petroleum and alcohol. The substance thus obtained is, however, not quite pure, but, on treatment with hydroxylamine, it readily yields pure *α-amyron-oxime*, $C_{30}H_{48}{:}NOH$, which crystallises from benzene in needles, and melts with evolution of gas at 233—234°. *β-Amyrone*, $C_{30}H_{48}O$, forms nodular aggregates of small prisms, melts at 178—180°, is readily soluble in chloroform, ether, and benzene, sparingly in light petroleum and alcohol; its *oxime*, $C_{30}H_{48}{:}NOH$, crystallises from benzene in long, pointed plates which melt with evolution of gas at 262—263°.

When α-amyrin acetate is subjected to the action of chromic acid in acetic acid solution, two atoms of hydrogen are replaced by one of oxygen with formation of *oxy-α-amyrin acetate*, $C_{30}H_{47}O{\cdot}OAc$, which crystallises from benzene in six-sided, rhombic plates ($a : b : c = 0{\cdot}6845 : 1 : 1{\cdot}2538$), melts at 278°, and is insoluble in alcohol and ether, sparingly soluble in acetic acid, readily in benzene. By the action of alcoholic potash, it is converted into *oxy-α-amyrin*, $C_{30}H_{47}O{\cdot}OH + 2H_2O$, which melts at 207—208°, and forms acicular crystals readily soluble in alcohol, ether, and benzene, insoluble in light petroleum; the 2 mols. H_2O are slowly evolved at 100°. Its solutions in alcohol and benzene, like those of bromo-β-amyrin, solidify to jellies on cooling.

β-Amyrin acetate, on oxidation, appears to behave in a manner similar to the α-compound, but the oxy-β-amyrin acetate could not be obtained free from unaltered β-amyrin acetate.

The oxygen atom in these compounds is not present in the form of a hydroxyl or carbonyl group, for oxy-α-amyrin acetate is not acted on by acetic anhydride or hydroxylamine; it is therefore probably present in the same form as in the alkylene oxides. A similar compound was obtained by Schrötter (Abstr., 1882, 66) by the oxidation of borneol acetate.

The alcohols related to amyrin appear to be widely distributed in the vegetable kingdom. Liebermann's cholesterin reagent (acetic

anhydride and concentrated sulphuric acid) gives strongly coloured solutions with almost all amyrin derivatives, the bromine compounds giving a blue, and the others a violet or purple-red, coloration. Lævo-α-amyrilene gives only a yellowish, or, at most, pink, coloration.

H. G. C.

Pectin Substances. By A. Herzfeld (*Chem. Centr.*, 1891, ii, 618—619; from *Zeit. Verein Rübenzück. Ind.*, 1891, 667—678).—*Parapectic acid* was obtained by the author by heating 500 grams of sliced beetroot with 1000 grams of water and 50 c.c. of concentrated hydrochloric acid at 70° for one hour. The liquid was separated from the solid portion, neutralised with sodium carbonate, and precipitated with alcohol. The substance thus obtained was not quite free from mineral matter, and contained 29·6 per cent. of mucic acid and 4 per cent. of furfuraldehyde. Parapectic acid appears to consist of a mixture of substances which yield arabinose and galactose.

Metapectic acid was obtained both from the sliced roots and from parapectin by treatment with calcium carbonate. The specimens thus obtained differed in their optical properties, the one being dextrorotatory, whilst the other was lævo-rotatory, and the amounts of mucic acid and furfuraldehyde obtained from each were not the same.

J. W. L.

First Product of the Reduction of Nitro-compounds with Tin and Hydrochloric Acid, or with Stannous Chloride. By E. Hoffmann and V. Meyer (*Ber.*, **24**, 3528—3535).—It was observed long ago that, in preparing normal butylamine by the reduction of nitrobutane with tin and hydrochloric acid, there is formed a considerable quantity of a substance which reduces Fehling's solution. The authors' recent experiments have shown that other fatty nitro-compounds, such as nitromethane, nitroethane, and secondary nitropropane, show a like behaviour, but that nitrobenzene and nitrophenol do not yield any substances which have a reducing action on Fehling's solution. It was also found that when nitromethane (1 mol.) is treated with pure stannous chloride (1 mol.) in concentrated hydrochloric acid solution, methylamine hydrochloride, ammonium chloride, and β-methylhydroxylamine hydrochloride, NHMe·OH,HCl, are formed; the three compounds are best separated by fractionally precipitating the alcoholic solution of the mixed products with dry ether.

These experiments show that the conversion of nitromethane into methylamine takes place in the following two phases:—$CH_3{\cdot}NO_2 + 2H_2 = H_2O + NHMe{\cdot}OH$ and $NHMe{\cdot}OH + H_2 = H_2O + NH_2Me$, and that the reduction of the Fehling's solution is due to the formation of a hydroxylamine derivative.

F. S. K.

Isomerism of Oximes. By G. Minunni (*Gazzetta*, **21**, ii, 192—205).—The author replies to Hantzsch's criticisms (Abstr., 1891, 823) on his explanation of the isomerism of oximes (Abstr., 1891, 1354). The conversion of the β-oximes into nitriles is readily explained by supposing the formation of a nitroso-derivative as an intermediate product. The intramolecular change noted by Beckmann can

also be explained in a somewhat similar manner. To the argument that three, and not two, isomeric oximes are accounted for by the author's hypothesis, it is replied that the stereochemical hypothesis is, in many cases, open to the same objection. Finally, the author's hypothesis is in no way dependent on the presence of the benzene nucleus, but only requires the compound to contain the group X=C–C=X; as this group is contained in the oximes of succinic acid, the isomerism existing among them is satisfactorily explained. W. J. P.

Action of Oxidising Agents on Aliphatic Thiocarbamides. By D. S. Hector (*J. pr. Chem.* [2], **44**, 492—506; compare Abstr., 1889, 872; 1890, 526).—When thiocarbamide is heated with hydrogen peroxide in hydrochloric acid solution, it is decomposed with the formation of ammonium chloride, sulphur, sulphuric acid, and carbonic anhydride.

Pseudothiocyanogen, $HC_3N_3S_3$, was the ultimate product of the action of hydrogen peroxide on ammonium thiocyanate in hydrochloric acid solution; it did not dissolve in alcohol, but dissolved readily in potassium hydroxide solution, from which it was precipitated by hydrochloric acid; the alkaline solution gave a yellowish-brown precipitate with silver nitrate.

Allylthiocarbamide is decomposed when heated with hydrogen peroxide in neutral solution, and subsequently with barium hydroxide, with formation of sulphuric acid, formic acid, allylamine, and ammonia.

Allylformamidine bisulphide, $S_2[C(NH\cdot C_3H_5):NH]_2$, is prepared by heating allylthiocarbamide with hydrogen peroxide ($\frac{1}{2}$ mol. proportion) in an acid solution. After filtering off the sulphur, separating sulphuric acid by barium hydroxide, and the excess of the latter by carbonic anhydride, the liquid is evaporated, until a viscid oil separates on cooling. The oil is dried on the water-bath, and cooled in a desiccator, when it sets to a vitreous mass, the analysis of which points to the above formula. The new base is bivalent; it dissolves readily in hot water, but sparingly in cold, and these solutions turn red litmus blue; it also dissolves in alcohol, but not in ether, benzene, or chloroform. It decomposes when heated. Its salts do not crystallise, but are very soluble in water. An aqueous solution of the bisulphide gives a white precipitate with silver nitrate, which rapidly becomes black; it is also precipitated by platinic chloride, mercuric chloride, picric acid, potassium ferrocyanide, and potassium ferricyanide. When it is heated with barium hydroxide, ammonia and allylamine are evolved. The *sulphate*, $C_8H_{14}N_4S_2,H_2SO_4 + H_2O$, forms a viscous, white mass, but does not crystallise; the *picrate*, $C_8H_{14}N_4S_2,2C_6H_3N_3O_7$, forms yellow granules, which melt at 178—180°; the *platinochlorides*, $C_8H_{14}N_4S_2,H_2PtCl_6 + 2H_2O$ and $(C_8H_{14}N_4S_2,2HCl)_3(PtCl_4)_2$, were both obtained; the *mercurochloride*, $C_8H_{14}N_4S_2,4HgCl_2$, is a white, crystalline powder, and melts at 171—172°.

Diallyldithiotetrahydrotriazole, $NH<\begin{matrix}CS\cdot N\cdot C_3H_5\\ |\\ CS\cdot N\cdot C_3H_5\end{matrix}$.—This compound is obtained by dropping a solution of potassium nitrite (4 grams) into

a solution of allylthiocarbamide (5 grams) acidified with sulphuric acid; the solution is afterwards shaken with ether, and the ethereal solution washed with dilute sodium hydroxide solution, dried, and evaporated. It is a yellow oil, insoluble in water and dilute acids, but soluble in alcohol and ether; it is a feeble base, giving precipitates with platinic chloride, silver nitrate, mercuric chloride, and copper sulphate. The *platinochloride*, $(C_8H_{11}N_3S_2)_2.H_2PtCl_6$, was obtained.

Dimethyldithiotetrahydrotriazole, $NH<\begin{matrix}CS\cdot NMe\\ |\\ CS\cdot NMe\end{matrix}$ is prepared in like manner, and is a yellow oil, giving similar reactions. A. G. B.

Constitution of Caprylaldehyde. By A. Béhal (*Bull. Soc. Chim.* [3], **6**, 131—137).—Substances having the formula $C_8H_{16}O$ have been prepared by the author in four different ways: (1) by the distillation of castor-oil soap; (2) by oxidation of capryl alcohol obtained by the distillation of castor-oil soap in presence of an alkali; (3) by the action of zinc methyl on œnanthylic chloride; (4) by the addition of the elements of water to true acetylenic caprylidene.

All these substances have the same odour, and boil at 171—172°; their densities at 0° are respectively: (1) 0·8331; (2) 0·8337; (3) 0·8399, 0·8387; (4) 0·8399.

The smaller values obtained in the first two cases are probably due to the presence of a little capryl alcohol. None of these compounds reduce ammoniacal silver nitrate in alcoholic solution. The products are identical, and by the third method of preparation the substance must be a methyl ketone. This is substantiated by the preparation of the oxime, which boils at 218°, and, on treatment with acetic chloride, yields an acetyl-derivative, which gives barium acetate and the original ketone when distilled with baryta.

The products of oxidation of the compound prepared in each of the four ways are caproic and acetic acids. The caproic acid obtained has been prepared in large quantity and purified. The fraction passing over at 204—206° readily crystallises from methyl chloride; it fuses at −10·5°, a point much lower than that indicated by Fittig for the normal acid (*Annalen*, **200**, 49), but this difference is, perhaps, due to a trace of impurity.* Its density at 0° is 0·9456. The calcium salt crystallises in plates containing 1 mol. H_2O. The solubility of this salt is such that at +1° the solution contains 2·084 grams of the anhydrous salt per 100 c.c., and at 23·5° the corresponding amount is 2·852 grams. These numbers correspond with the determinations of the solubility of the calcium salt of normal caproic acid made by Lieben and Rossi.

The so-called caprylaldehyde is therefore normal methyl hexyl ketone. W. T.

Dry Distillation of Organic Silver Salts. By W. Koenigs (*Ber.*, **24**, 3589—3590).—The author points out that the decomposition of organic silver salts when heated frequently takes a course

* The difference between the temperature of fusion found, −10·5°, and that given for the normal acid, −2°, would require as much as 2 per cent. of an impurity of low molecular weight, such as water, for its production, according to Raoult's law.—*Note by Abstractor.*

quite different from that studied by Kachler (this vol., p. 37). He quotes a number of well-known cases in which the silver salt is decomposed, with evolution of carbonic anhydride, yielding considerable quantities of a substance of which the acid in question is a carboxyl-derivative. F. S. K.

Glycocine and its Derivatives. By B. Goldberg, P. Kunz, and K. Kraut (*Annalen*, **266**, 292—310; compare Mauthner and Suida, Abstr., 1891, 38).—Amidoacetic acid (glycocine) is best prepared by gradually adding a concentrated aqueous solution of chloracetic acid to a large excess of concentrated ammonia with constant stirring, and, after keeping for 24 hours, expelling the excess of ammonia, first with a stream of air, and then by warming on the water-bath; the acid is isolated by means of its copper salt. The mother liquors from the copper salt contain di- and tri-glycolamidic acid (compare Heintz, *Annalen*, **122**, 257; **124**, 297), but 20—30 per cent. of the chloracetic acid is converted into products other than those already named, the nature of which could not be determined. The *barium* salt, $(NH_2{\cdot}CH_2{\cdot}COO)_2Ba + 4H_2O$, is obtained in small, lustrous crystals when the acid (1 part) and crystalline barium hydroxide (2 parts) are dissolved in a little water, the filtered solution poured into alcohol, and the precipitated oil left for some days in contact with the supernatant liquid; it melts at about 42°, and cannot be obtained in an anhydrous condition. The *strontium* salt, with $1\frac{1}{2}H_2O$, *calcium* salt, with H_2O, and the *magnesium* salt, with $2H_2O$, were prepared in like manner, and are all crystalline; the calcium salt loses the whole of its water at 105—110°, and its aqueous solution has a strongly alkaline reaction. These experiments prove the inaccuracy of Curtius' statements regarding the non-existence of such salts. A double *salt* of the composition

$$\begin{matrix} HO{\cdot}CH_2COO \\ NH_2{\cdot}CH_2{\cdot}COO \end{matrix}\!\!>\!Zn + 2H_2O$$

is formed by the union of molecular proportions of zinc amidoacetate and zinc glycollate; it is a crystalline compound, sparingly soluble in cold, and decomposed by hot water with separation of zinc oxide.

When methyl amidoacetate hydrochloride is boiled with excess of copper oxide, it is completely decomposed, yielding methyl alcohol, copper amidoacetate, and cupric chloride; ethyl amidoacetate hydrochloride, under the same conditions, is decomposed in a similar manner. There is, therefore, no reason for supposing that in these compounds copper can be substituted for the hydrogen of the amido-group (compare Curtius and Goebel, Abstr., 1888, 576), and it is probable that all the metallic derivatives of amidoacetic acid are formed by the substitution of the hydrogen of the carboxyl group. F. S. K.

Diethylamidocaproic Acid. By E. Duvillier (*Bull. Soc. Chim.* [3], **6**, 90—92).—Normal α-bromocaproic acid (1 mol.) is heated in sealed tubes at 100° with excess of diethylamine (3 mols.) in concentrated aqueous solution. The base is recovered by boiling with baryta, the baryta precipitated exactly with sulphuric acid, and the

product treated with silver oxide. A little dissolved silver is removed by hydrogen sulphide, and the solution evaporated to a syrup, from which the pure amido-acid is obtained by conversion into the copper salt, which is deposited on evaporation at a low temperature as a violet salt, accompanied by a small quantity of a green salt, and is purified by crystallisation from aqueous solution over sulphuric acid; the copper diethylamidocaproate is then decomposed by hydrogen sulphide. The acicular crystals of the copper salt are of a dark-violet colour, resembling that of chrome alum; they give fine, violet solutions in water and alcohol, their solubility in the latter being much the greater.

The free acid, $\cdot CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NEt_2) \cdot COOH$, is very soluble in water and alcohol, but insoluble in ether. Its solutions, when strongly concentrated, give a crystalline mass which decomposes on distillation. The *hydrochloride* is a syrupy substance, soluble in all proportions in water and alcohol.

The *platinochloride* is deposited from very concentrated aqueous solutions in orange-red, monoclinic prisms; it is very soluble in water, and soluble in alcohol, but insoluble in pure, dry ether. Ether precipitates it from its alcoholic solution as an orange-coloured oil. It contains 1 mol. H_2O, which it loses at 110°. The corresponding *aurochloride* is almost insoluble in water; it is deposited as a yellow oil from hot solutions, forming small, crystalline plates on cooling. The crystals are anhydrous, very soluble in alcohol, also soluble in pure, dry ether.

The green copper compound accompanying the copper diethylamidocaproate is copper hydroxycaproate; it yields barium hydroxycaproate on treatment with barium sulphide. The barium salt crystallises with $\frac{1}{2}$ mol. H_2O in brilliant needles, forming radiating groups.

W. T.

Derivatives of Isocrotonic Acid. By P. Melikoff and P. Petrenko-Kritschenko (*Annalen*, **266**, 358—378).—When a slight excess of hypochlorous acid is gradually added to an aqueous solution of isocrotonic acid, and the solution then extracted with ether, a thick, acid syrup is obtained, which consists of β-chlor-α-hydroxybutyric acid (m. p. 85—86°), small quantities of α-chloro-β-hydroxybutyric acid (m. p. 62—63°), the formation of which is probably due to the presence of crotonic acid, and α-chloro-β-hydroxybutyric acid (m. p. 80·5°).

The β-chlor-α-hydroxybutyric acid (m. p. 85—86°) is easily isolated by means of its sparingly soluble zinc salt (compare Abstr., 1884, 1301); the other two acids form readily soluble zinc salts and are separated from one another by means of their potassium salts, that of the α-chloro-β-hydroxy-acid (m. p. 62—63°) being much the more readily soluble in alcoholic ether.

α-Chloro-β-hydroxybutyric acid (m. p. 80·5°), prepared from its potassium salt, crystallises from ether in well-defined, rhombic prisms, and is readily soluble in water, alcohol, and ether. The *potassium* salt, $C_4H_6ClO_3K + 1\frac{1}{2}H_2O$, crystallises from hot 96 per cent. alcohol in long, silky, efflorescent prisms, and is readily soluble in water, but only sparingly in cold 96 per cent. alcohol. The *sodium* salt,

$C_4H_6ClO_3Na$, separates from hot alcohol in small, granular crystals, and seems to decompose at 70°. The *calcium* salt, *zinc* salt, and *silver* salt are amorphous. When the acid is distilled with concentrated sulphuric acid, it is converted into α-chlorocrotonic acid (m. p. 99°).

β-Methylisoglycidic acid, isomeric with the β-methylglycidic acid obtained from α-chloro-β-hydroxybutyric acid (m. p. 62—63°), is formed when α-chloro-β-hydroxybutyric acid (m. p. 80·5°) is treated with hot alcoholic potash, and the crystalline potassium salt decomposed with dilute sulphuric acid; it is a thick liquid, having a strong odour of butyric acid. The *potassium* salt, $C_4H_5O_3K + H_2O$, separates from alcoholic ether in prismatic crystals, melts at 82°, and is readily soluble in water and cold alcohol. The *silver* salt, $C_4H_5O_3Ag$, crystallises from hot water in small, colourless needles.

A *β-chlor-α-hydroxybutyric acid*, melting at 125°, and isomeric with the β-chlor-α-hydroxy-acid (m. p. 85—86°) referred to above, is obtained when the potassium salt of β-methylisoglycidic acid is treated with very concentrated hydrochloric acid; it crystallises in prisms and is readily soluble in water, ether, and alcohol. The *calcium* salt, $(C_4H_6ClO_3)_2Ca + 4H_2O$, is crystalline; the *zinc* salt, $(C_4H_6ClO_3)_2Zn$, crystallises in well-defined, transparent plates, and is readily soluble in water. When the acid is treated with alcoholic potash, it is reconverted into β-methylisoglycidic acid; on boiling a solution of its sodium salt, carbonic anhydride, propaldehyde, and sodium chloride are formed.

When α-chloro-β-hydroxybutyric acid (m. p. 80·5°) is heated with concentrated hydrochloric acid at 100°, it yields a dichlorobutyric acid (m. p. 72—73°), identical with the compound obtained from α-chloro-β-hydroxybutyric acid (m. p. 62—63°) in like manner.

β-Methylisoglyceric acid, $C_4H_8O_4$, is formed when β-methylisoglycidic acid is heated with water at 100° for 5—6 hours in sealed tubes; it crystallises in short, seemingly rhombic prisms, melts at 45°, and is readily soluble in alcohol and water, but only sparingly in ether. The *potassium* salt, $C_4H_7O_4K + H_2O$, crystallises from alcohol in prismatic plates, and is readily soluble in water. The *barium* salt, $(C_4H_7O_4)_2Ba + 2H_2O$, is a granular, crystalline compound. The *silver* salt, $C_4H_7O_4Ag$, crystallises from water, in which it is only sparingly soluble, in large prisms. When the acid is repeatedly melted, its melting point rises, possibly because it is partially converted into β-methylglyceric acid (m. p. 80°).

The authors are of the opinion that the chlorhydroxy-acids obtained from isocrotonic acid are the geometrical isomerides of the corresponding crotonic acid derivatives, and that their experiments afford additional proof of the structural identity of crotonic and isocrotonic acids.

F. S. K.

Preparation of Dehydracetic Acid. By H. v. Pechmann (*Ber.*, **24**, 3600).—Dehydracetic acid can be very conveniently prepared by treating acetonedicarboxylic acid with acetic anhydride, dissolving the crystalline substance (m. p. 154°) obtained in this way in dilute soda (1 mol.), evaporating to dryness, and then precipitating the aqueous solution of the residue with acetic acid; the yield is about 300 grams from 1 kilo. of citric acid.

F. S. K.

Resolution of Inactive Lactic Acid by Penicillium Glaucum. By G. Linossier (*Bull. Soc. Chim.* [3], **6**, 10—12).—After three months, solutions of ammonium lactate (corresponding with 5 per cent. lactic acid) in which pure cultivations of *Penicillium glaucum* have been growing become alkaline and lævogyrate. From the products the author has isolated a dextrogyrate lactic acid, which yields a lævogyrate zinc salt. Mixtures of hot solutions of this salt and of dextrogyrate zinc paralactate deposit, on cooling, crystals of inactive zinc lactate.

During the first two months, when the mould is vigorously growing, no active acid appears; it is only in its later stages of development, when fat appears in its hyphæ, that the nutrient solution manifests optical activity. Hence it appears that the healthy fugus attacks both varieties of lactic acid equally, but, when weakened, the lævorotatory variety is more easily assimilated. T. G. N.

Decomposition of Glutaric Acid at a High Temperature. By W. Lossen (*Annalen*, **266**, 264—266).—A reply to Claus (this vol., p. 40).—The author does not deny that carbonic anhydride is evolved when glutaric acid is heated under certain conditions; his and Wisbar's experiments (Abstr., 1891, 1011) were undertaken simply in order to ascertain whether, and if so which, butyric acid is formed on heating glutaric acid; they found that butyric acid is not produced, and, consequently, Claus' original statement is untrue.

F. S. K.

Conversion of Unsaturated Acids into their Stereochemical Isomerides by Soda. By A. Delisle (*Ber.*, **24**, 3620—3622).—Maleïc acid undergoes no change when it is heated with aqueous or alcoholic potash for a short time at 100°, as has lately been shown by Skraup (Abstr., 1891, 1338). The author finds that 30 per cent. soda is also without action at 100°, but that when the temperature is raised to 106°, the maleïc acid is slowly transformed into fumaric acid; malic acid is converted into fumaric acid under the same conditions.

When a solution of citraconic acid (6·5 grams) in 28 per cent. soda (100 c.c.) is heated for six hours on the water-bath, it yields mesaconic acid (3·7 grams) and itaconic acid (1·2 grams), but a considerable quantity of citraconic acid remains unchanged; when mesaconic acid (6·5 grams) is treated in like manner, it gives citraconic acid (1·8 grams) and itaconic acid (1 gram), a large quantity (3·7 grams) remaining unchanged.

Pyrocinchonic acid is not acted on by concentrated soda at 100°, but diphenylmaleïc acid is converted into a substance which melts considerably above 250°, and which seems to have the same percentage composition as diphenylmaleïc anhydride. F. S. K.

$\alpha\beta$-Dimethylglyceric Acid from Angelic Acid. By P. Melikoff and P. Petrenko-Kritschenko (*Annalen*, **226**, 378—380).—When the liquid dimethylglyceric acid obtained from angelic acid (Abstr., 1890, 862) is kept for a long time, it gradually solidifies to a mass of

crystals; this crystalline acid is identical with the $\alpha\beta$-dimethylglyceric acid obtained from tiglic acid. F. S. K.

Derivatives of Glutamic Acid. By A. Menozzi and G. Appiani (*Rend. Acad. Linc.*, **7**, i, 33—40).—Glutamic acid, prepared by the method of Hlasiwetz and Habermann, melts at 200°, and in aqueous solution (2—4 per cent.) has a specific rotatory power $[\alpha]_D = +12{\cdot}5°$ at 22°. For the hydrochloride in aqueous solutions (4 per cent.) $[\alpha]_D = +27{\cdot}5°$ at 15°, and for the calcium salt $[\alpha]_D = -3{\cdot}6°$ at 16°. These results agree fairly with those of Scheibler (Abstr., 1884, 1308). The authors were unable to prepare the diammonium salt described by Habermann (*Annalen*, **179**, 248).

Glutimide is best prepared by passing dry hydrogen chloride into a solution of glutamic acid (20 grams) in absolute alcohol (100 grams); the ethyl glutamate hydrochloride thus obtained is decomposed by moist silver oxide, and the dissolved silver precipitated by hydrogen sulphide; on concentration, ethyl glutamate separates, and, after being recrystallised from dilute alcohol, is converted into glutimide by heating in a closed tube with alcoholic ammonia for 7—8 hours at 140°. Or an alcoholic solution of glutamic acid may be saturated with hydrogen chloride, alcoholic ammonia added, the solution filtered from ammonium chloride, saturated with ammonia, and then heated in a closed tube for conversion into glutimide. The glutimide thus obtained is optically inactive, and crystallises without water of crystallisation in the oblique system, $a : b : c = 1{\cdot}403 : 1 : 1{\cdot}421$; $\beta = 86° 58'$.

Active *glutimide*, $C_5H_8N_2O_2$, is prepared by saturating the solution of ethyl glutamate obtained as above with ammonia in the cold; after some time glutimide separates, and, on recrystallisation from water, is obtained in large, orthorhombic prisms or tables ($a : b : c = 0{\cdot}661 : 1 : 1{\cdot}016$) containing 1 mol. H_2O, which is lost on drying over sulphuric acid or on heating at 100°. It melts at about 165°, and its specific rotatory power $[\alpha]_D = -140°$ in aqueous solution (8·5 per cent.) at 15°. The aqueous solution is not changed by boiling with magnesia, but readily yields ammonia when boiled with hydroxides of the alkalis or alkaline earths. The anhydrous compound dissolves in 13 parts of water at 9°, and in 125 parts of absolute alcohol at 13°. When heated with alcoholic ammonia in a closed tube for 8—9 hours at 140—150°, it is completely converted into inactive glutimide.

On treating inactive glutimide with concentrated hydrochloric acid, ammonium chloride and inactive *glutamic acid hydrochloride* are obtained. The latter substance forms orthorhombic crystals ($a : b : c = 0{\cdot}8852 : 1 : 0{\cdot}3866$), part of which show right-handed and part left-handed hemihedrism; it is therefore a mixture of the hydrochlorides of dextro- and lævo-glutamic acid.

On boiling the aqueous solution of inactive glutimide with barium hydroxide, precipitating with sulphuric acid, and concentrating the filtrate, inactive glutamic acid is obtained in orthorhombic crystals. These crystals are completely holohedral, but, on repeated crystallisation from water, crystals showing right- and left-handed hemihedrism are obtained. W. J. P.

A New Isomeride of Galactonic Acid and of Mucic Acid. By E. Fischer (*Ber.*, **24**, 3622—3629).—When galactonic acid is heated with quinoline or, better, with pyridine, it is partially converted into a stereochemical isomeride, which bears the same relationship to galactonic acid as gluconic does to mannonic acid; this new compound, which the author names talonic acid, yields, on reduction, a syrupy sugar (talose), which is converted into talomucic acid, the stereochemical isomeride of mucic acid, on oxidation with nitric acid.

Talonic acid is prepared by heating a 50 per cent. aqueous solution of pure galactonic acid (125 grams) with pyridine (125 grams) and water (1 litre) for two hours at 150° in a closed vessel; the filtered solution is boiled with crystalline barium hydroxide (125 grams) until free from pyridine, mixed with a quantity of sulphuric acid exactly sufficient to precipitate the barium, treated with animal charcoal, neutralised with cadmium carbonate and cadmium hydroxide, and filtered. On cooling, the sparingly soluble cadmium salt of galactonic acid is deposited in crystals; after separating this compound as completely as possible, the diluted mother liquors are treated with hydrogen sulphide, and the talonic acid in the hot, filtered solution precipitated with basic lead acetate. The colourless basic salt obtained in this way is decomposed with hydrogen sulphide, the filtered solution, which still contains galactonic acid, boiled with brucine and evaporated to a syrup; the brucine salt of talonic acid, which is deposited in crystals on cooling, is washed with a little alcohol and then dissolved in hot methyl alcohol, from which it separates in slender crystals melting at 130—133°, and readily soluble in water. The yield of the pure salt is 23 per cent. of the galactonic acid employed, which is equivalent to 7 per cent. of talonic acid. The free acid is obtained by boiling an aqueous solution of the brucine salt with barium hydroxide, evaporating the cold filtered solution to dryness, and extracting the residual barium salt with boiling alcohol to free it from brucine; if now the barium salt is decomposed with sulphuric acid in the usual way, and the filtrate evaporated, there remains a syrup which consists of a mixture of talonic acid and its lactone; this syrup is strongly dextrorotatory, and is readily soluble in hot alcohol. The *calcium*, *strontium*, *barium*, and *zinc* salts of the acid are very readily soluble in water, and do not crystallise. The *cadmium* salt, $(C_6H_{11}O_7)_2Cd + H_2O$, is a colourless, crystalline compound, very readily soluble in cold water. The *hydrazide*, $C_6H_{11}O_6{\cdot}N_2H_2Ph$, crystallises from hot alcohol in small, colourless prisms, melts at about 155° with slight decomposition, and is much more readily soluble in water than the corresponding derivative of galactonic-acid.

Talose, prepared from the mixture of the acid and its lactone in the usual manner, is a colourless syrup; its *hydrazone* differs from that of galactose in being very readily soluble in water, but its *osazone* cannot be distinguished from the corresponding galactose derivative.

When talonic acid is heated with pyridine under the conditions described above, it is partially converted into galactonic acid.

Talomucic acid, $C_6H_{10}O_8$, is obtained when talonic acid is evaporated with dilute nitric acid, and is purified by means of its calcium salt. It crystallises from acetone in colourless, microscopic, quadratic plates,

melts at about 158° with decomposition, and is very readily soluble in cold water and warm alcohol, but only sparingly in warm acetone, and almost insoluble in ether, chloroform, and benzene; its specific rotatory power is $[\alpha]_D^{20} = +29{\cdot}4°$ (approximately), but this value rapidly decreases on boiling the solution, owing to the formation of the lactone; it does not reduce Fehling's solution even on boiling. Aqueous solutions of the acid give colourless precipitates with lead acetate and with barium hydroxide, and in neutral solutions, cadmium sulphate produces a colourless precipitate. The *silver* salt is insoluble, and is decomposed by boiling water. The *potassium hydrogen* salt is a colourless syrup, very readily soluble in water. The *calcium* salt, $C_6H_8O_8Ca$, separates from hot water in the form of a colourless, crystalline powder; when boiled with water, it changes to a pasty mass, and only dissolves to a slight extent, but it is more readily soluble in hot, very dilute acetic acid. The *phenylhydrazide* crystallises in almost colourless plates, melts at 185—190° with decomposition, and is much more readily soluble in water than the dihydrazide of mucic acid. When talomucic acid is heated with concentrated hydrochloric and hydrobromic acids at 150°, it is converted into dehydromucic acid; on treatment with pyridine and water at 140°, it gives mucic acid. F. S. K.

Constitution of the Hydroxamic Acids. By F. Tiemann (*Ber.*, **24**, 3447—3453).—The reactions by which the hydroxamic acids are formed suggest at once that they are hydroxamido-derivatives of the general formula R·CO·NH(OH); the hydrogen of the hydroxyl group being displaceable by alkyl and alkoyl radicles. Lossen at first put forward this view, but he has since expressed the belief that they are oximido-derivatives of the general formula R·C(NOH)·OH on the ground that they are convertible into compounds containing either an oximido-group or an alkylated or alkoylated oximido-group. Thus, when treated with silver nitrate in alkaline solution, silver derivatives are formed which, on subsequent treatment with alkyl iodides, yield the compounds R·C(NOR′)·OR′, but Tafel and Enoch have shown (Abstr., 1890, 491) that certain aromatic amides, under similar conditions, yield compounds analogous to the last mentioned, thus, R·C(NH)·OR′, from which it might with equal force be urged that these amides had the constitution R·C(NH)·OH. The author is inclined to ascribe these phenomena to tautomerism, and he holds the opinion that the hydroxamic acids have the constitution R·CO·NH·OH. A. R. L.

Alkyl and Acidyl Sulphides. By S. H. Davies (*Ber.*, **24**, 3548—3552).—A compound of the composition Me_3IS is obtained when methyl bisulphide or methyl tersulphide is heated at 100° for 3—4 hours with methyl iodide; it crystallises in colourless needles, and, after having been converted into the corresponding chloride, gives a *platinochloride* of the composition $(Me_3SCl)_2,PtCl_4$.

Acetic sulphide (thiacetic anhydride), SAc_2, prepared by heating acetic acid with phosphorus pentasulphide, boils at 66—67° under a pressure of 20 mm., and at 156—158° under a pressure of 747·5 mm.,

with partial decomposition; when heated with water, it is decomposed into acetic acid and thiacetic acid. F. S. K

Thio-derivatives of Furfuraldehyde. By E. Baumann and E. Fromm (*Ber.*, **24**, 3591—3599; compare Abstr., 1891, 1008).—*α-Trithiofurfuraldehyde*, $(C_5H_4SO)_3$, and the *β*-compound described below, are produced when an alcoholic solution of furfuraldehyde is carefully mixed with alcoholic hydrochloric acid at −5°, and then saturated with hydrogen sulphide in the cold; after keeping for 24 hours, excess of sodium carbonate is added, the precipitate separated by filtration, dried in a desiccator, and dissolved in benzene or chloroform; on adding alcohol to the solution, the *β*-compound is for the most part precipitated, the *α*-compound remaining in solution. *α*-Trithiofurfuraldehyde is obtained in colourless crystals when the brown alcoholic benzene mother liquors are shaken with animal charcoal, the solution evaporated, and the residue repeatedly recrystallised from dilute alcohol; it melts at 128°, turns yellowish-brown on exposure to the air, and is very readily soluble in benzene and chloroform, but rather more sparingly in alcohol, and insoluble in water. Molecular weight determinations by Raoult's method in naphthalene solution gave results agreeing with those required by a compound of the molecular formula given above.

β-Trithiofurfuraldehyde, $(C_5H_4SO)_3$, is obtained in colourless needles when the precipitate referred to above is repeatedly recrystallised from benzene, using animal charcoal; it is formed when the *α*-compound, in benzene solution, is treated with ethyl iodide containing a trace of free iodine. It melts at 229° with decomposition, turns yellow on exposure to the air, and is readily soluble in chloroform, but more sparingly in benzene, and almost insoluble in alcohol; molecular weight determinations showed that the compound has the molecular formula assigned to it above.

The polymeride of thiofurfuraldehyde described by Cahours (*Annalen*, **69**, 85) is deposited in colourless crystals when an alcoholic solution of furfuraldehyde is treated with alcoholic ammonium sulphide at the ordinary temperature; it softens at 80°, melts completely at 90—91°, and has the empirical formula C_5H_4SO. Its molecular weight was determined by Raoult's method in naphthalene solution, and found to be about 2200, a result which corresponds approximately with the molecular formula $(C_5H_4SO)_{20}$; as, however, the depression of the freezing point of the naphthalene increases continuously with the time during which the solution is heated, it seems likely that the molecule is even greater than that given above, probably $(C_4H_5SO)_{24}$. It is readily soluble in benzene, and if ethyl iodide containing free iodine is added to the solution, *β*-trithiofurfuraldehyde is deposited in crystals after some time. When heated at a temperature just below 160° for 10—12 hours, it yields large quantities of the furfurostilbene described by Cahours and Schwanert; this compound is also obtained when either of the trithiofurfuraldehydes is heated at about 230°; it melts at 101°, and has the molecular formula $C_{10}H_8O_2$, as was proved by molecular-weight determinations in glacial acetic acid solution. F. S. K.

Constitution of Tetrole Nuclei. By G. Ciamician and A. Angeli (*Gazzetta*, **21**, ii, 109—133).—The authors' views of the constitution of tetrole nuclei have been lately expounded by Ciamician (Abstr., 1891, 1195), and in the case of thiophen are greatly supported by the following experiments, showing that derivatives of that substance on oxidation yield open chain compounds containing the group —CO·C:C·CO—.

Synthetical tetrabromothiophen (1 part), on treatment with nitric acid (sp. gr. 1·52, 10 parts), cooled in a mixture of snow and salt, is converted into a brown, semi-solid substance; on withdrawing the cooling mixture, this dissolves with development of heat, bromine being liberated, and on pouring the product into cold water, a white, crystalline compound separates which, however, soon redissolves. After being nearly neutralised with caustic alkali, extracted with ether, and the latter evaporated, dibromomaleïc anhydride is left, the yield being almost theoretical. It melts at 117—118°, and not at 114—115° as previously stated.

Tetrabromothiophen (3 grams), on oxidation in boiling acetic acid solution (50 c.c.) with chromic anhydride (5 grams), gives off bromine and yields a yellowish product which is insoluble in most of the ordinary solvents. On boiling with alcohol, and crystallising from boiling xylene, yellow scales are obtained which darken at 240°, and do not melt at 310°; this compound probably has the composition $C_9Br_4S_2O_2$. It dissolves in boiling caustic potash, yielding a brown solution, and with alcoholic potash gives a solution which is yellow while hot, and brown when cold. On heating the compound with phenylhydrazine, either directly or in solution in xylene or acetic acid, amorphous, highly-coloured products are obtained. On concentrating the xylene mother liquors from the crystallisation of the substance, a yellow, amorphous substance is obtained which is soluble in benzene, and melts at 220°; it is possibly a decomposition product of the less soluble substance.

Synthetical α-methyltribromothiophen (1 part) is gradually introduced into nitric acid (sp. gr. 1·52, 10 parts) cooled in snow and salt; it immediately dissolves to a reddish-brown liquid, but bromine is not evolved. If the solution is now poured into water (60 parts), the excess of acid partly neutralised by an alkali hydroxide, and the solution extracted with ether, the ether on evaporation leaves an oily residue; when this is suspended in water, and again extracted with ether, a yellow oil is obtained which solidifies after a time; by dissolving the product in warm benzene, precipitating by light petroleum, and crystallising it from benzene, colourless, orthorhombic prisms, $a : b : c = 0{\cdot}6381 : 1 : 0{\cdot}4670$, of *dibromoacetylacrylic acid* are obtained melting at 78—79°. This acid dissolves in solutions of the alkali carbonates with effervescence, is very soluble in hot water, ether, and alcohol, sparingly in cold water and benzene, and insoluble in light petroleum; on reduction with 2·5 per cent. sodium amalgam in dilute sulphuric acid solution, it yields dibromolevulinic acid. With phenylhydrazine in acetic acid solution, a deposit of yellow needles is obtained; this, after crystallisation from dilute alcohol, melts at 84—100°, and is probably a mixture.

β-Methyltribromothiophen (1 part), when dissolved in nitric acid (sp. gr. 1·52, 10 parts), and treated in a manner similar to the above, yields a yellow oil which soon solidifies. If this is dissolved in benzene, decolorised by animal charcoal, and precipitated several times by light petroleum, bromocitraconic anhydride is obtained melting at 100—101°, a slightly higher temperature than has previously been given.

Experiments on the oxidation of 2 : 5-dimethyldibromothiophen and 2 : 5-methylphenyltribromothiophen led to no positive result, the oxidation products being badly characterised.

The above experiments show the great analogy existing between the thiophen, pyrroline, and furfuran nuclei, and also afford a method of determining the position of the alcohol radicles in substituted thiophen derivatives.

The speed at which the oxidation proceeds was determined by allowing nitric acid of known strength to act on the thiophen derivative for a fixed time, interrupting the reaction, and estimating the sulphuric acid produced. Nitric acid of sp. gr. 1·47, acting for 18 minutes, decomposed 2·92 per cent. of tetrabromothiophen, 84·62 per cent. of α-methyltribromothiophen, and 72·00 per cent. of β-methyltribromothiophen; acid of sp. gr. 1·45, acting for 51 minutes, converted 24·14 per cent. of α-methyltribromothiophen and 31·12 per cent. of β-methyltribromothiophen. W. J. P.

Derivatives of Ethyl Acetothienoneoxalate. By S. Salvatori (*Gazzetta*, **21**, ii, 268—294).—Acetothienoneoxalic (thenoïlpyruvic) acid, obtained by Angeli (Abstr., 1891, 550) by the action of sulphuric acid on the ethyl derivative, may conveniently be prepared by treating a mixture of acetothienone and ethyl oxalate with sodium ethoxide, proceeding according to Brömme and Claisen's method of preparing benzoylpyruvic acid (Abstr., 1888, 691). The *ethyl* derivative, $C_4SH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}COOEt$, described by Angeli, gives rise to a series of metallic salts; the *copper* salt, $(C_{10}H_9SO_4)_2Cu$, forms a very insoluble, pale-green mass; the *ammonium* salt, $C_{10}H_{10}SO_4,2NH_3$, is obtained as a pale salmon-coloured, crystalline powder soluble in alcohol, benzene, and ethyl acetate. It melts at 125° with decomposition, and its solutions evolve ammonia on heating to 60—70°. No nitroso-derivative could be obtained either from the acid or from the ethyl derivative by V. Meyer's method, the product consisting of α-thiophenic acid.

Thienylphenylpyrazolic Acid, $\begin{matrix}CH{\cdot}C(COOH)\\ \|\\ C(C_4SH_3){\cdot}NPh\end{matrix}\!\!>\!N$.—The ethyl derivative of this acid is formed by the condensation of a molecule of ethyl acetothienoneoxalate with a molecule of phenylhydrazine with elimination of 2 mols. H_2O. It crystallises from alcohol in colourless, monoclinic prisms, $a : b : c = 1{\cdot}177 : 1 : 0{\cdot}716$; $\beta = 64°\,10'$, melts at 81°, dissolves in most solvents, but not in water. The acid is obtained from the ethereal salt by hydrolysis. It separates from alcohol in triclinic crystals, melts at 195°, and decomposes at a slightly higher temperature; the *silver* salt, $C_{14}H_9AgSN_2O_2$, forms a white, curdy

mass; salts of copper, mercury, zinc, lead, barium, and iron have also been prepared. On heating it above its melting point, it loses carbonic anhydride, and yields the corresponding *thienylphenylpyrazole*, $C_{13}H_{10}SN_2$. The latter crystallises from alcohol in white needles, melts at 54°, and distils unaltered above 300°. It is freely soluble in alcohol, ether, and benzene, and sparingly in water; it is dissolved by concentrated mineral acids, and reprecipitated on dilution; it gives Knorr's reaction for pyrazoles.

The *ethiodide*, $C_{13}H_{10}SN_2,EtI$, crystallises from water in colourless prisms melting at 173—174°; the *platinochloride*, $(C_{13}H_{10}SN_2)_2,H_2PtCl_6$, separates in dark orange-yellow flakes.

Thienylisoxazolic Acid, $\begin{matrix}CH\cdot C(COOH)\\ \|\\ C(C_4SH_3)-O\end{matrix}\!\!>\!N$.—The ethyl derivative of this acid was prepared by Angeli by the condensation of ethyl acetothienoneoxalate with hydroxylamine. The free acid may be obtained in colourless crystals melting at 177° with decomposition, and readily soluble in alcohol, ether, and water. The silver salt, $C_8H_4AgSNO_3$, separates in white flakes; salts of copper, lead, mercury, barium, and iron were also prepared.

A hydrated *oxime* of acetothienoneoxalic acid, $C_8H_7SNO_4 + H_2O$ may be prepared by dissolving the acid in a slight excess of sodium carbonate, and adding the theoretical quantity of hydroxylamine, also dissolved in sodium carbonate, the solutions being kept so dilute that 30—40 c.c. of the liquid only contain 1 gram of acid; the mixture is then allowed to remain for some time. On acidifying with hydrochloric acid, the oxime gradually separates in minute crystals. It may be obtained pure by allowing a cold ethereal solution to evaporate spontaneously, and collecting the first crop of prismatic crystals deposited. It melts with decomposition at 110—112°, and dissolves in most solvents, but is partially converted into thienylisoxazolic acid. The conversion is more speedily effected by the action of acetic anhydride, no acetyl derivative being formed. This compound is of interest as being the first of the monoximes of the β diketonic acids which has been isolated.

Cyanacetothienone, $C_4H_3S\cdot CO\cdot CH_2\cdot CN$, is prepared by heating small quantities of thienylisoxazolic acid in a narrow tube until the evolution of carbonic anhydride ceases, and treating the residue with sodium carbonate. When pure, it crystallises from alcohol in colourless, lustrous plates, and from water in large needles, melts at 137°, and does not decompose at 200°. It resembles cyanacetophenone generally in its properties.

An *oxime* of benzoylpyruvic acid, $C_{10}H_9NO_4 + H_2O$, may be obtained by the method adopted for the preparation of acetothienoneoxalic oxime; but if the digestion with hydroxylamine is prolonged for more than three hours, the oxime formed at first is gradually converted into phenylisoxazolic acid. It bears a general resemblance to the preceding oxime, but is even more unstable; it melts at 98—100° with decomposition, and crystallises from its cold ethereal solution in prisms.

When phenylisoxazolic acid is heated above its melting point in

the manner described for the preparation of cyanacetothienone, the product is identical with the cyanacetophenone described by Haller (Abstr., 1886, 440). The formation of these nitriles shows that the constitution of the oximes may be respectively represented by the formulæ $C_4SH_3{\cdot}CO{\cdot}CH_2{\cdot}C(NOH){\cdot}COOH$ and $CH_2Bz{\cdot}C(NOH){\cdot}COOH$. The author believes that the behaviour of these oximes, and especially the high temperatures necessary for the formation of the nitriles, indicates that they are α-monoximes, and hence form an exception to Hantzsch's hypothesis. S. B. A. A.

Use of Sodium Hypophosphite in Sandmeyer's Reaction. By A. Angeli (*Gazzetta*, **21**, ii, 258—261).—Sandmeyer's original reaction has the disadvantage of involving the use of cuprous salts which are not very stable and must be freshly prepared. Gattermann's modification (Abstr., 1890, 970) involves the preparation of finely-divided copper perfectly free from zinc, and necessitates the constant agitation of the liquid, especially at the commencement of the reaction. The following process obviates these difficulties; it depends on the circumstance that when a solution of copper sulphate and sodium hypophosphite is acidified with hydrochloric acid and gently warmed, cuprous chloride speedily separates according to the equation $2CuCl_2 + H_3PO_2 + H_2O = H_3PO_3 + 2HCl + Cu_2Cl_2$ (Abstr., 1886, 771). A mixture of copper sulphate and sodium hypophosphite may therefore be added to acid solutions instead of cuprous salts or metallic copper. Aniline is, for example, converted into chloro-, bromo-, iodo-, and nitro-benzene as follows:—

Chlorobenzene.—A solution of aniline (9·3 grams) in hydrochloric acid (40 grams) and water (60 grams) is slowly mixed with a solution of sodium nitrite (7 grams), and then with a solution of copper sulphate (12·5 grams) and sodium hypophosphite (7 grams), when a brisk effervescence ensues, owing to the evolution of nitrogen; as soon as this is over, the product is steam-distilled, and the chlorobenzene separated and rectified. It passes over almost entirely at 132°, and is converted by concentrated nitric acid into parachloronitrobenzene melting at 183°.

Bromobenzene can be prepared in like manner by treating a solution of aniline (9·3 grams) in sulphuric acid (40 grams) and water (90 grams) with a solution of sodium nitrite (7 grams), allowing the mixture to remain for a while, then adding sulphuric acid (20 grams) diluted with water, and solutions of potassium bromide (36 grams), copper sulphate (12·5 grams), and sodium hypophosphite (7 grams).

Iodobenzene may be prepared in like manner.

Nitrobenzene is obtained by mixing a solution of diazobenzene nitrate acidified with nitric acid with solutions of copper sulphate and sodium hypophosphite, and gently warming.

The yields are very good, and the operations speedily performed. The reaction is also available for the preparation of cuprous bromide and iodide in a state of purity. S. B. A. A.

Displacement of the Nitro-group by Chlorine or Bromine. By C. A. Lobry de Bruyn (*Ber.*, **24**, 3749—3750).—When the

dinitrobenzenes are treated with chlorine or bromine in the absence of any substance that can act as a carrier of the halogen, the reaction does not begin until the temperature of 200° is reached.

With chlorine, orthodinitrobenzene yields dichlorobenzene; exceedingly little, if any, orthochloronitrobenzene is formed. Metadinitrobenzene yields metachloronitrobenzene and dichlorobenzene. Paradinitrobenzene yields parachloronitrobenzene only.

With bromine, the three dinitrobenzenes yield the corresponding bromonitrobenzenes; the further action of bromine leads to the substitution of bromine for hydrogen. An oxychloride or oxybromide of nitrogen is always formed in the reactions described. C. F. B.

Dithiocarbonic Acids. By G. Daccomo (*Chem. Centr.*, 1891, ii, 532—533; from *Ann. Chim. Farm.*, **13**, 273—280).—Bearing in mind the fact that potassium ethoxide and carbon bisulphide react with formation of potassium xanthate, the author studied the reaction between potassium hydroxide and carbon bisulphide. Solid potassium hydroxide, left in contact with carbon bisulphide, reacts gradually; the bisulphide becomes coloured at first yellow, which deepens into red, and, finally, a reddish-brown mass is produced. After washing with alcohol and drying over sulphuric acid, a crystalline, reddish-brown powder is obtained, which is readily soluble in water. With dilute acids, it is decomposed with formation of hydrogen sulphide, carbonic anhydride, carbon oxysulphide, and sulphur. With salts of the metals, precipitates are formed; and with diazo-derivatives, compounds are produced similar to those obtained by Leuckart with potassium xanthate. With diazobenzene nitrate, two new compounds, the one crystalline and the other liquid, are formed. Both have the empirical formula COS_2Ph_2, and are phenyl dithiocarbonates. In order to determine which has the formula OPh·CS·SPh, and which the formula $CO(SPh)_2$, the author treated both with alcoholic potash. The following reactions would take place:—

$$OPh{\cdot}CS{\cdot}SPh + 2KOH = PhSH + PhOH + K_2CO_2S.$$
$$CO(SPh)_2 + 2KOH = 2PhSH + K_2CO_3.$$

In neither case, however, was the formation of phenol observed, nor was there any carbon oxysulphide liberated from the product by treatment with acid; only thiophenol and potassium carbonate could be detected. It is suggested, therefore, that a molecular change takes place in the one or the other during hydrolysis, as Solomon has already noticed in the case of the hydrolysis of ethyl xanthate.

By treating the crystalline product of the action of potassium hydroxide on carbon bisulphide with metachlorodiazobenzene, a reddish-brown oil, *chlorophenyl dithiocarbonate*, is obtained which also gradually separated into a crystalline and a liquid portion, and these both react with alcoholic potash, forming potassium carbonate and metachlorothiophenol. Paradiazotoluene behaves in an exactly similar manner. J. W. L.

Metachlorothiophenol. By G. Daccomo (*Chem. Centr.*, 1891, ii, 533—534; from *Ann. Chim. Farm.*, **13**, 343—352).—The author has

carefully examined the metachlorothiophenol mentioned in the preceding abstract, since it differs from the one obtained by Otto from chlorobenzenesulphonic chloride. The method of preparation was as follows:—Nitrobenzene was treated with chlorine in presence of iodine, according to Laubenheimer's method (*Ber.*, **8**, 1621). It was reduced with fuming hydrochloric acid and tin, and a very pure metachloraniline boiling at 230—232° was obtained. From this, the corresponding diazochlorobenzene was formed by the action of potassium nitrite. Lastly, the metachlorodiazobenzene was treated with potassium dithiocarbonate, yielding chlorophenyl dithiocarbonate, from which metachlorothiophenol was obtained by hydrolysis.

Chlorophenyl dithiocarbonate is a dark-coloured oil, readily soluble in ether, benzene, chloroform, and carbon bisulphide, sparingly soluble in alcohol, and insoluble in water. It may be distilled in a current of steam, but it is readily decomposed by heating. Potassium xanthate reacts with metachlorodiazobenzene in a similar manner to the dithiocarbonate.

Metachlorothiophenol is a colourless, limpid liquid which refracts light strongly, and has an especially penetrating odour. It is insoluble in water, but readily soluble in alcohol, ether, chloroform, and carbon bisulphide. It is readily soluble in alkalis, and is precipitated from the solutions by acids. Its sp. gr. is 1·2637 at 12·5°. The ethereal solution reacts with mercuric oxide, and a thick, crystalline mass of the mercury salt is formed. The neutral solutions of the potassium or sodium salts precipitate solutions of lead salts, light yellow; copper salts, dirty yellow; mercury salts, white; silver nitrate, yellow. With concentrated sulphuric acid, no reaction takes place in the cold, but, on warming, a beautiful, light violet coloration suddenly appears.

With chloral, a chemical change is indicated by the development of heat, but no definite product could be separated. The potassium salt, C_6H_4ClSK, consists of small, prismatic, colourless needles, readily soluble in water, sparingly so in alcohol; the barium salt, $(C_6H_4ClS)_2Ba$, consists of shining scales, little soluble in water; the mercury salt, $(C_6H_4ClS)_2Hg$, pearly scales, almost insoluble in water and alcohol. All the salts have the characteristic odour of metachlorothiophenol.

With acid chlorides, metachlorothiophenol reacts readily, hydrogen chloride being liberated, and the corresponding salt produced. The *acetyl* derivative, C_6H_4ClSAc, is a colourless, strongly refractive liquid which distils between 255° and 268°. The *benzoyl* derivative, C_6H_4ClSBz, forms triclinic prisms melting at 72·5°. J. W. L.

Ortho- and Para-chlorothiophenol. By G. Daccomo (*Chem. Centr.*, 1891, ii, 656—657; from *Ann. Chim. Farm.*, **14**, 1—13).—The author has obtained ortho- and para-chlorothiophenols by the same method as that employed for the preparation of the meta-derivative.

Parachlorophenyl dithiocarbonate, obtained from diazochlorobenzene chloride, prepared from parachloraniline, forms white, pearly scales, which are readily soluble in most organic solvents, but the compound

does not melt at a definite temperature. The author considers it possible that it is a mixture of the isomerides $CO(S\cdot C_6H_4Cl)_2$ and $C_6H_4Cl\cdot S\cdot CS\cdot OC_6H_4Cl$. If diazobenzene chloride is added to potassium xanthate instead of to the dithiocarbonate, the *chlorophenylxanthate*, $OEt\cdot CS\cdot S\cdot C_6H_4Cl$, is obtained; this forms white crystals which melt at 124—126° to a colourless liquid. By hydrolysing each of these compounds with alcoholic potash, *parachlorothiophenol*, $C_6H_4Cl\cdot SH$, is obtained, which possesses all the characteristics of Otto's compound (*Annalen*, **143**, 109). With sulphuric acid, it produces the same violet coloration as the meta-compound does.

Acetylparachlorothiophenol, obtained by the action of acetic chloride, is crystalline, readily soluble, and boils at 255° under ordinary atmospheric pressure. Its sp. gr. is 1·2629 at 19·5°. The benzoyl derivative forms large crystals, and melts at 75·5°.

Orthochlorothiophenol is prepared in an exactly similar manner from orthodiazochlorobenzene. It forms a colourless, strongly refractive liquid, of penetrating, but not disagreeable, odour; boils at 204—206°, and has sp. gr. 1·2752 at 19·5°. It resembles the meta-derivative in its reactions, but is less stable, and gradually evolves hydrogen sulphide with formation of chlorophenyl sulphide. The *acetyl* compound boils at 254—258°; sp. gr. 1·2659 at 19·5°. The *benzoyl* compound boils at 335—340°, sp. gr. 1·2785.

For the sake of comparison, the author prepared the three corresponding chlorophenols; the ortho- and para-compounds, by the action of dry chlorine on phenol at the ordinary temperature; the meta-compound according to the methods of Beilstein and Kurbatoff, and of Uhlemann. The following derivatives are described: *acetylorthochlorophenol*, liquid, boiling point 204—208°; sp. gr. 1·1709 at 19·5°. *Benzoylorthochlorophenol*, liquid, boiling point 308—312°; sp. gr. 1·1974 at 19·5°. *Acetylmetachlorophenol*, liquid, boiling point 226—228°; sp. gr. 1·2165. *Benzoylmetachlorophenol*, solid, melting point 71°. *Acetylparachlorophenol*, liquid, boiling point 230—232; sp. gr. 1·2404 at 19·5. *Benzoylparachlorophenol*, solid, melting point 87°.

J. W. L.

Action of Methylchloroform and Ethylchloroform on Alkaline Solutions of Phenols. By F. Heiber (*Ber.*, **24**, 3677—3687).—*Phenyl orthacetate*, $CMe(OPh)_3$, is obtained when methylchloroform (16·8 parts) is gradually added in the course of several days to a hot solution of phenol (38·4 parts) and sodium hydroxide (22·6 parts) in water (22·6 parts). It crystallises from hot alcohol in transparent plates, melts at 98—98·5°, and is readily soluble in ether, chloroform, and benzene, but almost insoluble in water; it dissolves in concentrated sulphuric acid with a red coloration, and on prolonged boiling with alcoholic potash, it is decomposed into phenol and acetic acid. The *tribromo*-derivative, $C_{20}H_{15}O_3Br_3$, is formed when phenyl orthacetate is treated with bromine in cold glacial acetic acid solution; it crystallises from hot alcohol in transparent plates, melts at 132—133°, is very stable towards acids and alkalis, and is moderately easily soluble in ether, chloroform, and benzene, but insoluble in water.

Orthonitrophenyl orthacetate, $CMe(O\cdot C_6H_4\cdot NO_2)_3$, prepared from methylchloroform and orthonitrophenol in like manner, melts at

167—168°, and is only sparingly soluble in most ordinary solvents with the exception of boiling benzene; it is very stable towards dilute acids and alkalis.

Paracresyl orthacetate, $CMe(O{\cdot}C_6H_4Me)_3$, crystallises from alcoholic ether in rhombic plates, melts at 135·5° (?), and is soluble in all the ordinary organic solvents, but insoluble in water; it is only slowly acted on by boiling acids and alkalis. The *tribromo*-derivative, $C_{23}H_{21}O_3Br_3$, separates from boiling acetic acid in crystals, melts at 160—161°, and is insoluble in water, but more or less readily soluble in all the ordinary organic solvents.

Metacresyl orthacetate, $C_{23}H_{24}O_3$, crystallises in needles, melts at 99—100°, and is insoluble in water, but readily soluble in ether, chloroform, and boiling alcohol; the *tribromo*-derivative, $C_{23}H_{21}O_3Br_3$, melts at 151·5—153°.

Orthocresyl orthacetate, $C_{23}H_{24}O_3$, forms transparent crystals, melts at 87·5—89°, and is readily soluble in all ordinary organic solvents, but only sparingly in water.

Resorcinyl orthacetate, $CMe(O{\cdot}C_6H_4{\cdot}OH)_3$, is a yellow powder, melts at about 155—159° with decomposition, and is readily soluble in cold alcohol, ether, and glacial acetic acid, but only sparingly in hot water, and insoluble in benzene.

Hydroxybenzophenone, $COPh{\cdot}C_6H_4{\cdot}OH$, is obtained, together with phenyl benzoate (m. p. 70·5—71·5°) and a yellowish-red, resinous substance, when an alkaline solution of phenol is warmed with benzotrichloride (phenylchloroform); it crystallises from dilute alcohol in colourless plates, melts at 41°, and is readily soluble in alcohol, ether, glacial acetic acid, and alkalis, but insoluble in water.

F. S. K.

Derivatives of Carvacrol. By G. Mazzara and G. Plancher (*Gazzetta*, **21**, ii, 155—157).—Paternò and Canzoneri obtained nitrosocarvacrol by the action of potassium nitrite on carvacrol, but the yield was very small; 70 per cent. of the theoretical may be obtained, however, by slowly dropping amyl nitrite (35 grams) into an ice-cold solution of carvacrol (50 grams), and soda (15 grams) in the smallest possible quantity of alcohol. The ethyl alcohol is eliminated by spontaneous evaporation, the solution diluted with much water, separated from the precipitated amyl alcohol and resin, and acidified with sulphuric acid. The nitrosocarvacrol, which separates, is dissolved in ammonia, reprecipitated with sulphuric acid, and finally crystallised from benzene.

Diacetylamidoethenylamidocarvacrol, $NAc_2{\cdot}C_6HMePr<\overset{O}{\underset{N}{>}}CMe$, is obtained by heating acetic anhydride with monacetylamidoethenylamidocarvacrol in molecular proportion at 180—190°; the excess of acetic anhydride is evaporated off, the product cooled to 60°, and washed with water. After recrystallisation from boiling alcohol, it is obtained in transparent tables which melt at 123—125°, and lose their transparency on exposure to light.

Acetyldinitrocarvacrol, $C_6H(NO_3)_2PrMe{\cdot}OAc$, is prepared by heating a mixture of dinitrocarvacrol with acetic chloride for some hours in a reflux apparatus. The product is washed with dilute sodium

carbonate solution, and dissolved in boiling alcohol; on cooling, it separates as an oil which soon solidifies. By crystallisation from light petroleum, it is obtained in yellowish rhombohedra, which turn red on exposure to light; it melts at 72—73°.

The acetyl and benzoyl derivatives of dinitrothymol melt at higher temperatures than those of dinitrocarvacrol, whilst the ethenyl and benzenyl derivatives of carvacrol melt at higher temperatures than the isomeric thymol derivatives. W. J. P.

Action of Dinitrochlorobenzene on Polyhydric Phenols. By R. Nietzki and B. Schündelen (*Ber*, **24**, 3585—3589).—*Tetranitrodiphenylresorcinol*, $C_6H_4[O\cdot C_6H_3(NO_2)_2]_2$, is formed when molecular proportions of resorcinol, sodium ethoxide, and chlorodinitrobenzene [Cl : $(NO_2)_2$ = 1 : 2 : 4] interact in alcoholic solution at the ordinary temperature. It crystallises from glacial acetic acid in almost colourless plates, melts at 184°, and is insoluble in alkalis, and only very sparingly soluble in most ordinary organic solvents; it seems to be completely decomposed by reducing agents, and when boiled with aniline, it yields dinitrodiphenylamine. On treatment with cold fuming nitric acid, it is converted into *pentanitrodiphenylresorcinol*, $C_{18}H_9N_5O_{12}$, but with a warm mixture of nitric and sulphuric acid, it yields the *hexanitro*-derivative, $C_{18}H_8N_6O_{14}$; the former melts at 68°, the latter at 220°, and both compounds are decomposed by boiling aniline with formation of dinitrodiphenylamine.

Tetranitrodiphenylquinol, $C_{18}H_{10}N_4O_{10}$, prepared from quinol in like manner, crystallises from glacial acetic acid in lustrous plates, melts at 240°, and is very sparingly soluble in most ordinary organic solvents; it is not decomposed by boiling aniline. Its *dinitro*-derivative, $C_{18}H_8N_6O_{14}$, crystallises from glacial acetic acid in almost colourless plates, and melts at 190°; its *trinitro*-derivative melts at 220°; both these compounds are decomposed by boiling aniline with formation of dinitrodiphenylamine.

Hydroxydinitrodiphenylamine, $C_{12}H_9N_3O_5$, is obtained by treating orthamidophenol with chlorodinitrobenzene in presence of sodium acetate; it crystallises in brownish-yellow needles, and melts at 190°.

Dihydroxydinitrodiphenylamine, $C_{12}H_9N_3O_6$, prepared from amidoresorcinol in like manner, crystallises in brown needles, and melts at 183°. F. S. K.

Oxidation of Aromatic Compounds containing the Side Chain C_3H_5. By G. Wagner (*Ber.*, **24**, 3488—3491).—When safrole is oxidised in the cold with a 1 per cent. solution of potassium permanganate, it yields the corresponding glycol, $C_{10}H_{12}O_4$, which crystallises from ether in prismatic needles, melts at 78·5°, and gives a diacetyl derivative boiling at 262° under a pressure of 90 mm. (compare Tiemann, this vol., p. 47). Besides the glycol, which, contrary to Tiemann's statement, is more soluble in cold alcohol than in boiling ether, piperonal, piperonylic, α-homopiperonylic, formic, and other acids are produced, but not acetic. When isosafrole is oxidised, it yields a glycol crystallising in thick prisms and melting at 101—102°. The glycol obtained from methyleugenol crystallises

in prismatic needles, melts at 68—69°, and gives a diacetyl derivative boiling at 248° (35 mm.); whilst the glycol from methylisoeugenol crystallises in rhombic plates and melts at 88°. A. R. L.

Myristicin and its Derivatives. By F. W. Semmler (*Ber.*, **24**, 3818—3823).—In a previous communication, the author has shown that myristicin has the composition $C_{12}H_{14}O_2$,, and is a derivative of benzene containing an unsaturated side chain (Abstr., 1890, 1150). To obtain further information as to its constitution, it was subjected to the action of oxidising agents; nitric acid and chromic acid act in too violent a manner, but the oxidation may be readily carried out by means of dilute potassium permanganate. The liquid is filtered hot from the manganese precipitate, allowed to cool, and the white, crystalline compound which separates collected and recrystallised several times from water. It has the composition $C_9H_8O_4$, melts at 130° (uncorr.), boils at 290—295°, reduces silver solution, and combines with hydroxylamine and phenylhydrazine. It is, therefore, an aldehyde $C_8H_7O_3{\cdot}CHO$, and may be termed *myristicinaldehyde;* it is also found to contain one methoxyl group, and, as already stated, is a derivative of benzene; the formula may therefore be further resolved into $CH_2O_2{\cdot}C_6H_2(OMe){\cdot}CHO$. The oxygen must be present in the form of an oxymethylene group, for neither myristicin nor myristicinaldehyde behaves as a phenol; hence myristicinaldehyde has the constitutional formula $CH_2{<}^{O}_{O}{>}C_6H_2(OMe){\cdot}CHO$, and occupies an intermediate position between piperonaldehyde, $CH_2{<}^{O}_{O}{>}C_6H_3{\cdot}CHO$, and apionaldehyde, $CH_2{<}^{O}_{O}{>}C_6H(OMe)_2{\cdot}CHO$. The constitution of myristicin itself is, therefore, $CH_2{<}^{O}_{O}{>}C_6H_2(OMe){\cdot}C_4H_7$, and it may be termed *oxymethylenemethoxybutenylbenzene.*

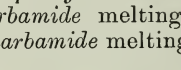
The filtrate from myristicinaldehyde contains the corresponding *myristic acid*, $CH_2{<}^{O}_{O}{>}C_6H_2(OMe){\cdot}COOH$, which separates in white, crystalline flakes on the addition of phosphoric acid, and, after recrystallisation from hot water, forms long, yellowish-white needles. It melts at 208—210° (uncorr.), does not boil without decomposition, even in a vacuum, and is only sparingly soluble in water.

In order to ascertain the positions occupied by the side chains in these compounds, myristic acid was heated with phosphorus and hydriodic acid in a sealed tube; the product of the reaction was found to be gallic acid, showing that the methoxyl and oxymethylene groups must occupy the positions 3 : 4 : 5, the carboxyl, aldehyde, or butenyl groups occupying the position 1.

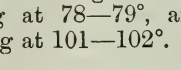
When myristicin is treated with bromine in acetic acid solution, carbonic anhydride is evolved, and a voluminous precipitate separates; this, after recrystallisation from alcohol, forms slender, snow-white needles, and melts at 159—160° (uncorr.). It has the composition $C_8H_5O_3Br_3$, and appears to be *methyloxymethylenetribromopyrogallol.* H. G. C.

Action of Carbonyl Chloride on Benzylamine. By B. Kühn and J. Riesenfeld (*Ber.*, **24**, 3815—3818).—Hitherto, benzyl isocyanate has not been prepared in the pure condition, the product obtained by acting on silver cyanate with benzyl bromide or chloride (this Journal, 1872, 446; *Ber.*, **10**, 46) always containing chlorine or bromine. The authors have endeavoured to prepare it by the action of carbonyl chloride on benzylamine hydrochloride; the product is, however, a mixture of varying quantities of benzyl isocyanate and benzylchloroformamide, $CH_2Ph{\cdot}NH{\cdot}COCl$, which cannot be separated by fractional distillation, nor can the latter derivative, like methylchloroformamide (Abstr., 1887, 569), be converted into the former by distilling with potash, benzyl cyanurate being thus obtained. The same compound is precipitated when a large quantity of light petroleum is added to the mixture of benzyl isocyanate and chloroformamide. When the mixture is treated with aniline, the sole product is phenylbenzylcarbamide; methylaniline converts it into *benzylphenylmethylcarbamide* melting at 84°, metanitraniline into *benzylmetanitrophenylcarbamide* melting at 188°, α-naphthylamine into *benzyl-α-naphthylcarbamide* melting at 203°, isobutylamine into *benzylisobutylcarbamide* melting at 78—79°, and piperidine into *benzylpiperidylcarbamide* melting at 101—102°. H. G. C.

Nomenclature of Stereoisomeric Nitrogen Compounds and of Rings containing Nitrogen. By A. Hantzsch (*Ber.*, **24**, 3479—3488).—The author proposes to distinguish the stereoisomeric nitrogen compounds by the Greek prefixes *syn*, *anti*, and *amphi*, these being equivalent to *cis*, *trans*, and *cistrans*, which are employed by v. Baeyer for certain other stereoisomeric compounds. The prefix *syn* is used with those compounds containing certain groups which are capable of intramolecular change, whilst *anti* is employed with the isomeride containing the same groups which are incapable of it; for example, *syn* is prefixed to that benzaldoxime from which benzonitrile is obtainable, thus:—

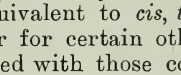


Synbenzaldoxime.

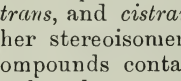


Antibenzaldoxime.

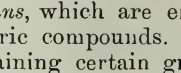
For distinguishing such compounds as the three isomeric benziledioximes, it is necessary to employ also the prefix *amphi*, as follows:—



Synbenzilediodioxime.



Antibenzilediodioxime.



Amphibenzilediodioxime.

The author is of opinion that the term "*azo*," in its application to closed-ring compounds, should be restricted to those containing triad nitrogen, whilst, for such as contain the group NH, the term "*imid*" should be employed. He proposes the following alterations in nomenclature:—*Imidole* for pyrroline, *thiole* for thiophen, and

oxole for furfuran; derivatives obtained by displacing a CH group in these by N are designated *imidazole* = $C_3H_3(NH)N$, *oxazole* = $C_3H_3(O)N$, and *thiazole* = $C_3H_3(S)N$ respectively. The isomerism of these compounds may then be indicated by the above-mentioned prefixes; thus, the two imidazoles [NH : N = 1 : 2 and 1 : 3] are called *synimidazole* and *amphimidazole* respectively, whilst Widman's triazoles, $C_2H_2(NH)N_2$, are named *imidodiazoles* or *azimidazoles*, and the three isomerides [$NH_2 : N_2$ = 1 : 2 : 5, 1 : 2 : 3, and 1 : 3 : 5] are distinguished as *synazimidazole*, *synimidodiazole*, and *amphimidodiazole*. The three six-membered ring compounds $C_4H_4N_2$ are designated *syndiazine*, *amphidiazine*, and *antidiazine*, according as they have the constitutions [N : N = 1 : 2, 1 : 3, and 1 : 4]. A. R. L.

Action of Benzyl Chloride on Ortho- and Para-toluidines. By C. Rabaut (*Bull. Soc. Chim.* [3], **6**, 137—140).—*Methylbenzylorthotoluidine*, $C_6H_4Me{\cdot}NMe{\cdot}CH_2Ph$, is obtained by heating a mixture, in molecular proportion, of benzylorthotoluidine and methyl iodide for 40 hours. The product is heated with dilute sodium carbonate and extracted with benzene. At 210—215°, under 15·2 mm. pressure, a yellowish oil passes over; this is insoluble in water, soluble in alcohol, benzene, &c., and has no basic character.

The sulphonic derivative of benzylorthotoluidine is obtained by heating benzylorthotoluidine for two hours at 125—130° with sulphuric acid containing 15 per cent. of anhydride; its lead and barium salts are soluble in water and crystallise well. The acid is a crystalline powder, soluble in water. Its aqueous solution, when treated with lead dioxide, becomes first green and then blue.

Benzylparatoluidine.—A mixture of paratoluidine (2 mols.) and benzyl chloride (1 mol.) is maintained at 155—165° for 40 hours. A yellowish oil is separated, as above; this distils at 205—215° under 10—15 mm. pressure, and darkens in colour on cooling. It remains liquid, even in melting ice, whereas the dibenzyl derivative melts at 54·5—55°, and benzoylorthotoluidine melts at 56—57°. The yield in the case of benzylorthotoluidine is 40 per cent., whilst in the case of benzylparatoluidine it is only 30 per cent. At a temperature higher than 170°, large quantities of a black, resinous product are formed; this does not distil up to 270° under 20 mm. pressure.

The salts of benzylparatoluidine are white and well crystallised, but little soluble in cold water, more soluble in, and readily decomposed by hot water. The methyl and ethyl derivatives of this base are obtained by heating it with the corresponding alcoholic iodides. *Benzylethylparatoluidine* is a yellow liquid boiling at 200—210° under 10 mm. pressure. *Benzylmethylparatoluidine* is a slightly yellow liquid boiling at 210—220° under 30 mm. pressure. These derivatives have no basic characters.

Benzoylbenzylparatoluidine.—This compound is formed by the action of benzoic chloride on benzylparatoluidine. The product, if distilled when hydrochloric acid ceases to be disengaged, yields a thick liquid, which passes over at 275—285° under a pressure of 20 mm., and rapidly solidifies. No salts have been obtained with acids. When dissolved in glacial acetic acid and added drop by drop to fuming nitric acid, a

nitro-derivative is obtained, which is precipitated by the addition of water. It dissolves in alcohol and crystallises in yellow needles, 1 cm. long, which melt at about 135—137°. It appears to consist of two substances, into which it separates on fusion; that in greater quantity melts at 135—137°. W. T.

Action of Benzyl Chloride on Metaxylidine. By Jablin-Gonnet (*Bull. Soc. Chim.* [3], **6**, 21).—A mixture of benzyl chloride (1 mol.) and metaxylidine (2 mols.) is heated in a reflux apparatus at 160—165° for 50 hours. The resulting crystalline mass is boiled with saturated sodium carbonate solution, and the oily, brown layer which separates is, after extraction with benzene, distilled under reduced pressure. *Benzylmetaxylidine*, $C_6H_3Me_2{\cdot}NHBz$, passes over at 200—210° under a pressure of 15 mm. as a pale yellow liquid, which is soluble in alcohol and benzene; with acids, it forms white, unstable salts, which are decomposed by water. Methyl, ethyl, and acetyl derivatives have been made and will be described later.

T. G. N.

Action of Hydroxylamine Hydrochloride on Acetomesitylene. By E. Feith and S. H. Davies (*Ber.*, **24**, 3546—3548).—Acetylmesidine (m. p. 216—217°) is formed, when an alcoholic solution of acetomesitylene is heated at 160° for six hours with hydroxylamine hydrochloride and sodium acetate, the oxime which is first produced immediately undergoing intramolecular change.

Acetophenone and acetopseudocymene are not acted on by hydroxylamine under the conditions just stated, but propiomesitylene, at a rather higher temperature (180°), yields, on prolonged heating, a very small quantity of a crystalline compound which melts at 154·5°, and is insoluble in potash. F. S. K.

Derivatives of Trinitroquinol. By R. Nietzki and H. Kaufmann (*Ber.*, **24**, 3824—3830).—Twelve years ago Nietzki showed that one of the nitro-groups in trinitrodiethylquinol may be readily replaced by an amido- or substituted amido-group; thus aniline yields a diethoxydinitrodiphenylamine. The latter, on boiling with alkali, was found to yield a substance having acid properties, which was regarded as diethyldinitrotrihydroxybenzene (Abstr., 1878, 866).

Further investigation has shown that this supposition is incorrect, the substance having the composition $C_{14}H_{13}N_2O_6$, instead of $C_{10}H_{12}O_7N_2$; it must, therefore, be formed by the hydrolysis of one of the ethoxy-groups, and is an *ethoxyhydroxydinitrodiphenylamine*,

$$OEt{\cdot}C_6H(OH)(NO_2)_2{\cdot}NHPh$$

[OEt : NHPh : NO_2 : OH : NO_2 = 1 : 2 : 3 : 4 : 5]. It crystallises from alcohol in yellow needles, and melts at 152°.

When diethoxydinitrodiphenylamine is reduced with tin and hydrochloric acid, it yields the corresponding *diethoxydiamidodiphenylamine*, $C_6H(OEt)_2(NH_2)_2{\cdot}NHPh$, which crystallises in almost colourless needles, and melts at 77°; its *hydrochloride*, $C_{16}H_{21}N_3O_3,2HCl$, forms colourless needles, which become blue on drying, and are less stable than the free base. On boiling with acetic anhydride, it yields a deriva-

tive which is simultaneously an acetyl compound and an anhydrobase, and has the constitution $NHAc{\cdot}C_6H(OC_2H_5)_2{<}\overset{NPh}{\underset{\quad N}{\quad}}{>}CMe$; it forms colourless needles, melts at 162°, and is readily soluble in hot water, alcohol, ether, and dilute acids.

Trinitrodiethylquinol also readily reacts with an excess of dimethylparadiamidobenzene, the reaction proceeding in the same manner as with aniline; the nitro-group is evolved as nitrous acid, and converts a portion of the diamine into dimethylaniline. The chief product of the action, which has the constitution

$$C_6H(NO_2)_2(OEt)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2,$$

has distinctly basic properties, and crystallises from alcohol in beautiful, red needles melting at 148°. Its *hydrochloride* forms needles which have a green surface lustre, and are decomposed by water. It is readily reduced by tin and hydrochloric acid, but the resulting triamido-compound cannot be isolated, as it rapidly undergoes oxidation; if manganese dioxide be added, and the mixture boiled till the original blue colour has changed to brown, the residue, on extraction with boiling alcohol, yields the product of oxidation in beautiful needles having a green lustre. The analysis showed that it has the composition $C_{18}H_{22}N_4O_2$, and it is, therefore, as would be expected from its mode of formation, a *diethoxydimethyldiamidophenazine*, $NH_2{\cdot}C_6H(OEt)_2{<}\overset{N}{\underset{N}{|}}{>}C_6H_3{\cdot}NMe_2$, and has all the properties of a eurhodine. It dissolves in concentrated sulphuric acid with a green colour, which, on dilution, passes through blue into red, and colours silk with a slightly violet-red nuance. The *picrate*,

$$C_{18}H_{22}N_4O_2,C_6H_3N_3O_7,$$

crystallises in needles having a green lustre; the *acetyl* derivative, $C_{18}H_{21}N_4O_2Ac$, crystallises in pale red needles melting at 179°, and yields red salts with acids.

Paradiamidobenzene does not undergo condensation with trinitrodiethylquinol so readily, but its acetyl derivative gives more satisfactory results; the product of the reaction forms yellow, silky needles, melts at 199°, and has the constitution $C_6H(OEt)_2(NO_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NHAc$. On boiling with dilute alkali, the acetyl group is not eliminated, but instead one of the ethyl groups is removed, with formation of a substance having the constitution $OH{\cdot}C_6H(OEt)(NO_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NHAc$, which forms yellowish-brown crystals, readily soluble in alcohol, and melts at 206°. More concentrated alkali converts it into a *dinitroethyltrihydroxybenzene*, $OEt{\cdot}C_6H(OH)_2(NO_2)_2$, which forms yellow needles, and melts at 210°; it is not identical with the dinitroethyltrihydroxybenzene obtained by Nietzki from diamidodinitrophenetoïl (Abstr., 1883, 466).

Trinitrodiethylquinol also undergoes condensation with dimethylmetadiamidobenzene and α-naphthylamine; the first yields a compound of slightly basic properties, having the constitution

$$C_6H(OEt)_2(NO_2)_2{\cdot}\underset{1}{NH}{\cdot}C_6H_4{\cdot}\underset{3}{NMe_2},$$

which crystallises in orange-yellow needles and melts at 106°. The compound obtained from α-naphthylamine,

$$C_6H(OEt)_2(NO_2)_2\cdot NH\cdot C_{10}H_7^{\alpha},$$

forms yellow needles melting at 128°, and may be separated from the α-amidoazonaphthalene simultaneously formed by taking advantage of its lesser solubility in alcohol. H. G. C.

Diazobenzene Perbromide. By C. E. Saunders (*Amer. Chem. J.*, **13**, 486—490).—On treating an aqueous solution of diazobenzene sulphate, best prepared by Knoevenagel's method (Abstr., 1891, 54), with an excess of cold solution of bromine in moderately strong hydrobromic acid, diazobenzene perbromide separates as a dark, pasty mass, which, when repeatedly washed with ether and dried between filter paper, loses most of its colour, and almost ceases to smell of bromine. The liquid product originally obtained by Griess (*Phil. Trans.*, 1864, 673), which was probably a mixture or compound of the perbromide with free bromine, may be formed by exposing the dry solid to bromine vapour, of which it absorbs a very large quantity; the perbromide may be recovered by treatment with ether. In the preparation of the perbromide, symmetrical tribromobenzene occurs as a bye-product; it is dissolved, however, by the ether.

When diazobenzene perbromide is treated with bromine-water, it yields tribromophenol, and when boiled with water alone, it yields in addition phenol, hydrogen bromide, and bromine. When boiled with alcohol, it gives, not bromobenzene alone, as stated by Griess (*loc. cit.*), but a mixture of this substance with parabromophenetoïl, melting at 4° (compare Remsen and Orndorff, Abstr., 1888, 268). With boiling ether and with glacial acetic acid, it yields bromobenzene, mixed, in the latter case, with another compound of much higher boiling point. Jn. W.

Intramolecular Formation of an Azo-group. By E. Lellmann and B. Arnold (*Ber.*, **24**, 3557—3560; compare Täuber, this vol., p. 183).—*Orthazodibenzylamine*, $NH<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$, is obtained when an alkaline solution of the theoretical quantity of stannous chloride is gradually added to a hot alcoholic solution of orthodinitrodibenzylamine; it crystallises in small, orange needles, melts at 230°, and is only very sparingly soluble in alcohol, but more readily in benzene. The *hydrochloride*, $C_{14}H_{13}N_3,HCl + H_2O$, crystallises in slender, orange needles, and is converted into the base when heated at 80°.

Paratolylorthazodibenzylamine, $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$, can be obtained from orthodinitrodibenzylparatoluidine in like manner. F. S. K.

Alkyl Derivatives of Hydroxylamine. By R. Kothe (*Annalen*, **266**, 310—323; compare Behrend and König, Abstr., 1891, 1032).—When α-benzylhydroxylamine is oxidised with potassium dichromate and glacial acetic acid, it yields benzyl alcohol and traces of benzyl nitrite and benzyl acetate, nitric oxide being evolved.

When α-dibenzylhydroxylamine is treated with potassium dichromate and sulphuric acid, it yields benzylbenzaldoxime and small quantities of benzaldehyde and benzoic acid; if the potassium dichromate is added very gradually to a very dilute sulphuric acid solution of the α-dibenzylhydroxylamine, the yield of benzylbenzaldoxime is much smaller, but benzyl alcohol and other compounds are formed in its place.

Tribenzylhydroxylamine is not acted on by potassium dichromate and sulphuric acid under the conditions employed by the author.

When tribenzylhydroxylamine is distilled under reduced pressure, it is decomposed into β-dibenzylhydroxylamine, stilbene, benzylamine, β-benzylhydroxylamine, and ammonia. F. S. K.

Amidoximes and Azoximes. By F. Tiemann (*Ber.*, **24**, 3648—3650).—General remarks on the papers of Marcus, Goldbeck, Paschen, and Richter. (Compare following abstracts.) F. S. K.

Nitrogenous Derivatives of some Aromatic Dihydroxyaldehydes. By E. Marcus (*Ber.*, **24**, 3650—3657).—*β-Resorcylaldoxime*, $C_6H_3(OH)_2\cdot CH{:}NOH$ [$CH : (OH)_2 = 1 : 2 : 4$], prepared from β-resorcylaldehyde, crystallises in colourless needles, melts at 191°, and is readily soluble in alcohol and ether; it gives with ferric chloride a brownish-red coloration, and with Fehling's solution a green precipitate. The corresponding hydrazone (m. p. 158—159°) was also prepared. (Compare Rudolph, Abstr., 1889, 251.)

Diacetyl-β-resorcylonitrile, $CN\cdot C_6H_3(OAc)_2$, is formed when the aldoxime is boiled with acetic anhydride; it crystallises from alcohol in colourless prisms, melts at 72°, and is readily soluble in alcohol, ether, chloroform, and benzene.

β-Resorcylonitrile, $C_7H_5NO_2$, is produced when the diacetyl derivative is hydrolysed with dilute potash. It separates from a mixture of ether and light petroleum in crystals, melts at 175°, and is readily soluble in water, alcohol, and ether; its aqueous solution gives a red coloration with ferric chloride.

β-Resorcenylamidoxime, $C_6H_3(OH)_2\cdot C(NH_2){:}NOH$, prepared by treating the nitrile with hydroxylamine at the ordinary temperature, turns brown at 160°, melts at 166°, and is readily soluble in water, alcohol, and ether; it reduces Fehling's solution, and gives a brown coloration with ferric chloride.

The *dioxime*, $(OH)_2C_6H_2(CH{:}NOH)_2$ [$(CH)_2 : (OH)_2 = 1 : 6 : 2 : 4$], is obtained when resorcyldialdehyde is treated with hydroxylamine; it melts at 209°, and is readily soluble in alcohol, ether, and potash, but only sparingly in water; in its aqueous solutions, ferric chloride produces a black, and copper sulphate a blue, precipitate.

Orthomethoxyparahydroxybenzophenylhydrazone, $C_{14}H_{14}N_2O_2$, prepared from the corresponding aldehyde, is a yellow, crystalline substance melting at 151—152°; it is readily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. The corresponding *aldoxime*, $C_8H_9NO_3$, melts at 171°, and is soluble in water, alcohol, ether, and soda, its solutions giving a brownish-red coloration with ferric chloride.

Acetylvanillonitrile, $CN\cdot C_6H_3(OMe)\cdot OAc$ [CN : OMe : OAc = 1 : 3 : 4], prepared by heating vanillinaldoxime (m. p. 117°) with acetic anhydride, crystallises from hot water in colourless needles, melts at 110°, and is soluble in alcohol, ether, and benzene.

Vanillonitrile, $C_8H_7NO_2$, is formed when the acetyl derivative is dissolved in cold, dilute potash; it crystallises from hot water in colourless needles, melts at 87°, and is soluble in alcohol, ether, and benzene. In its aqueous solution, ferric chloride produces a blue coloration, and, on warming, a crystalline substance is precipitated.

Vanillenylamidoxime, $C_8H_{10}N_2O_3$, prepared from the nitrile just described, crystallises from water in prisms, melts below 100°, and dissolves freely in alcohol, hydrochloric acid, and soda, but is only sparingly soluble in ether, and insoluble in benzene; in its aqueous solutions, ferric chloride produces a reddish-violet, and Fehling's solution a green, coloration.

Piperonalaldoxime, $CH_2<^{O}_{O}>C_6H_3\cdot CH{:}NOH$, crystallises from hot water in lustrous needles, melts at 110°, and dissolves freely in alcohol, ether, benzene, chloroform, and carbon bisulphide. The corresponding *nitrile*, $C_8H_5NO_2$, is readily soluble in alcohol, ether, and benzene, and crystallises from water in lustrous needles melting at 95°. The *amidoxime*, $C_8H_8N_2O_3$, melts at 151°, and is soluble in hot water, alcohol, ether, acids, and alkalis; its *hydrochloride*, $C_8H_8N_2O_3,HCl$, is a colourless, crystalline compound melting at 193°.

Ethenylpiperonenylazoxime, $CH_2<^{O}_{O}>C_6H_3\cdot C<^{NO}_{N}>CMe$, is formed when piperonenylamidoxime is heated with acetic anhydride; it melts at 110°, and is readily soluble in alcohol, ether, and benzene, but insoluble in water. F. S. K.

Nitrogenous Derivatives of Parahomosalicylic Acid. By O. Goldbeck (*Ber.*, **24**, 3658—3667).—*Parahomosalicylaldoxime*, $OH\cdot C_6H_3Me\cdot CH{:}NOH$ [Me : CH : OH = 1 : 3 : 4], crystallises in long, colourless needles, melts at 105°, and dissolves freely in hot water, alcohol, ether, chloroform, and benzene, but is only sparingly soluble in light petroleum and cold water; its aqueous solution gives a dirty violet coloration with ferric chloride.

Acetylparahomosalicylonitrile, $C_{10}H_9NO_2$, prepared by boiling the aldoxime with acetic anhydride, melts at 56—57°, and is readily soluble in alcohol, ether, benzene, acetone, chloroform, and hot light petroleum, but only sparingly in water.

Parahomosalicylamide, $C_8H_9NO_2$, obtained by heating ethyl parahomosalicylate with concentrated ammonia, crystallises from dilute alcohol in colourless needles, melts at 177—178°, and is readily soluble in alcohol and ether, but more sparingly in benzene and chloroform; its aqueous solution gives with ferric chloride a dark-violet coloration. The corresponding *thiamide*, C_8H_9NOS, was obtained in an impure condition by melting the amide with phosphorus pentasulphide; it dissolves freely in alcohol, ether, chloroform, benzene, alkalis, and hot water, melts at 126—127°, and gives with ferric chloride a dark-violet coloration, with copper sulphate a green,

and with silver nitrate a reddish-brown, precipitate. The *nitrile*, C_8H_7NO, is formed, with evolution of hydrogen sulphide, when the thiamide is submitted to dry distillation. It melts at 100—101°, dissolves freely in alcohol, ether, benzene, and chloroform, and is decomposed by boiling alkalis; in its aqueous solution, ferric chloride produces a violet coloration.

Parahomosalicenylamidoxime, $C_8H_{10}N_2O_2$, prepared by heating the thiamide with hydroxylamine in dilute alcoholic solution, crystallises from hot benzene in plates, and from hot water in needles, melting at 123—124°; it is readily soluble in ether, alcohol, hot water, and chloroform, and in its aqueous solution ferric chloride produces a reddish-violet coloration, and copper sulphate a light-green precipitate. The *hydrochloride* melts at 215° with decomposition. The *benzoyl* derivative, $C_{15}H_{14}N_2O_3$, obtained by triturating the amidoxime with benzoic chloride, melts at 181—182°, and is readily soluble in acetone, but only sparingly in alcohol, ether, and benzene, and insoluble in water and light petroleum; its alcoholic solution gives a green coloration with ferric chloride.

Benzenylparahomosalicenylazoxime, $OH\cdot C_6H_3Me\cdot C\ll^{NO}_{N}\gg CPh$, is formed when the benzoyl derivative (m. p. 181—182°) is heated with water at 100°; it melts at 151°, dissolves freely in ether, alcohol, chloroform, benzene, light petroleum, and alkalis, and gives with ferric chloride in alcoholic solution a green coloration.

Dibenzoylparahomosalicenylamidoxime, $C_{22}H_{18}N_2O_4$, prepared by shaking the amidoxime with potash and benzoic chloride, melts at 143°, and is readily soluble in hot alcohol, ether, chloroform, and benzene, but insoluble in water, acids, and alkalis.

Acetylparahomosalicenylamidoxime, $C_{10}H_{12}N_2O_3$, is obtained when the amidoxime is treated with acetic anhydride at the ordinary temperature; it crystallises from hot benzene in plates, melts at 148—149°, and dissolves freely in alcohol, ether, chloroform, benzene, dilute acids, and alkalis; its dilute alcoholic solution gives a violet coloration with ferric chloride.

Ethenylparahomosalicenylazoxime, $C_{10}H_{10}N_2O_2$, separates from ether in prismatic crystals, melts at 45°, and is readily soluble in ether, alcohol, benzene, chloroform, and alkalis, but insoluble in water and dilute acids; in its alcoholic solution, copper sulphate produces a reddish-brown precipitate, and ferric chloride a blue coloration.

Propenylparahomosalicenylazoxime-ω-carboxylic acid,

$$OH\cdot C_6H_3Me\cdot C\ll^{NO}_{N}\gg C\cdot CH_2\cdot CH_2\cdot COOH,$$

can be obtained by heating the amidoxime with succinic anhydride at about 115°. It crystallises from dilute alcohol in slender, colourless needles, melts at 103°, and is readily soluble in ether, benzene, and hot water, but more sparingly in chloroform, and insoluble in light petroleum; its aqueous solution gives a violet coloration with ferric chloride, and in its neutral solutions silver nitrate produces a colourless, crystalline precipitate. F. S. K.

Derivatives of Orthohomosalicylaldehyde and of Orthohomoparahydroxybenzaldehyde. By E. Paschen (*Ber.*, **24**, 3667—3675).—*Orthohomosalicylphenylhydrazone*,

$$OH\cdot C_6H_3Me\cdot CH:N_2HPh\ [Me : OH : CH = 1 : 2 : 3],$$

crystallises from alcohol in colourless, rhombic plates, melts at 95°, and turns greenish on exposure to the air; it is readily soluble in alcohol, ether, and chloroform, but more sparingly in hot water, and insoluble in light petroleum. The *aldoxime*, $C_8H_9NO_2$, crystallises in long, colourless needles, melts at 99°, and dissolves freely in hot water, alcohol, ether, benzene, and chloroform, but is insoluble in light petroleum and cold water; in its aqueous solutions, ferric chloride produces a violet coloration, and Fehling's solution a brownish-red precipitate.

Orthohomosalicylonitrile, C_8H_7NO, is obtained when the aldoxime is boiled with acetic anhydride, and the oily product decomposed with cold, dilute soda; it crystallises from hot alcohol in colourless plates, melts at 88·5°, and is readily soluble in alcohol, ether, benzene, chloroform, and hot water, but insoluble in light petroleum.

Orthohomosalicenylamidoxime, $C_8H_{10}N_2O_2$, crystallises from alcohol in large, colourless plates, melts at 126·5°, and is insoluble in light petroleum; it dissolves freely in alcohol, benzene, chloroform, and hot water, and gives a dirty-green precipitate with Fehling's solution. The *dibenzoyl* derivative, $C_{23}H_{16}N_2O_4$, separates from alcohol in small, colourless needles, melts at 164°, and is readily soluble in ether, benzene, and chloroform, but insoluble in light petroleum and cold water.

Benzenylorthohomosalicenylazoxime, $C_{15}H_{12}N_2O_2$, prepared by boiling the dibenzoyl derivative (m. p. 164°) with soda, forms colourless needles, and melts at 150°; it is insoluble in light petroleum, but dissolves freely in most of the other ordinary organic solvents.

Orthohomoparahydroxybenzophenylhydrazone, $C_{14}H_{14}N_2O$, melts at 151°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in hot water, and insoluble in light petroleum. The *aldoxime*, $C_8H_9NO_2$, crystallises in colourless needles, and melts at 143·5°; it gives with ferric chloride a dark-green, and with Fehling's solution a light-green, coloration.

Acetylorthohomoparahydroxybenzonitrile, $C_{10}H_9NO_2$, is formed when the aldoxime (m. p. 143·5°) is boiled with acetic anhydride; it crystallises in colourless plates, melts at 75—76°, and is insoluble in light petroleum, but readily soluble in ether, alcohol, benzene, and chloroform. The *nitrile*, C_8H_7NO, prepared by hydrolysing the acetyl derivative with dilute soda, crystallises in colourless needles, melts at 93°, and resembles the preceding compound in its behaviour with solvents.

Orthohomoparahydroxybenzenylamidoxime, $C_8H_{10}N_2O_2$, forms colourless scales, melts at 152° with decomposition, and turns bluish-grey on exposure to the air; it is readily soluble in alcohol, but more sparingly in ether and hot water, and insoluble in benzene and light petroleum; it gives a bluish-green coloration with Fehling's solution. The *hydrochloride*, $C_8H_{10}N_2O_2,HCl$, crystallises in needles.

Ethenylorthohomoparahydroxybenzenylazoxime, $C_{10}H_{10}N_2O_2$, prepared by heating the amidoxime with acetic anhydride, crystallises from hot, dilute alcohol in small, colourless needles, melts at 89°, and is insoluble in water and light petroleum, but readily soluble in alcohol, ether, benzene, and chloroform. F. S. K.

β-Trichloro-α-hydroxypropenylamidoxime. By E. Richter (*Ber.*, **24**, 3676—3677).—*β-Trichloro-α-hydroxypropenylamidoxime*, $CCl_3{\cdot}CH(OH){\cdot}C(NH_2){:}NOH$, can be obtained by treating the nitrile of trichlorolactic acid with an aqueous solution of hydroxylamine at the ordinary temperature; it crystallises from hot water in plates, melts at 145° with decomposition, and is almost insoluble in benzene and ether, but more readily in alcohol. The *hydrochloride*,

$$C_3H_5N_2Cl_3O_2,HCl,$$

crystallises in plates.

Ethenyl-β-trichloro-α-hydroxypropenylazoxime,

$$CCl_3{\cdot}CH(OH){\cdot}C\ll^{NO}_{N}\gg CMe,$$

prepared by warming the amidoxime with acetic anhydride, crystallises from hot water in needles, melts at 160—161°, and is readily soluble in alcohol and ether, but only sparingly in benzene. F. S. K.

Phenylglyoximes. By A. Russanow (*Ber.*, **24**, 3497—3511).—*Antiphenylamphiglyoxime*, $\begin{matrix}Ph{\cdot}C & ---- & C{\cdot}H\\ \| & & \|\\ N{\cdot}OH & & N{\cdot}OH\end{matrix}$, is best prepared by treating sodioisonitrosoacetophenone (1 mol.) with hydroxylamine hydrochloride (1 mol.) and sodium hydroxide (1 mol.) in aqueous solution at the ordinary temperature (compare Scholl, Abstr., 1891, 287); the product is precipitated with acetic acid, washed with chloroform, and recrystallised from ether. It melts at 168°, is almost insoluble in chloroform, and is identical with the phenylglyoxime previously described by Schramm (*Ber.*, **16**, 2186) and by Strassmann (Abstr., 1889, 610).

Phenylantiglyoxime, $\begin{matrix}Ph{\cdot}C & - & C{\cdot}H\\ \| & & \|\\ OH{\cdot}N & & N{\cdot}OH\end{matrix}$, is precipitated, as hydrochloride, when hydrogen chloride is passed into an ethereal solution of the preceding compound; this salt is stable in dry air, but in a moist atmosphere it is quickly converted into the glyoxime with elimination of hydrogen chloride. This glyoxime is also formed when isonitrosoacetophenone is treated with hydroxylamine hydrochloride in dilute alcoholic solution; it crystallises in well-defined prisms melting at 180°. It is stable in acid solution, but it is very readily converted into its isomeride (m. p. 168°) by most ordinary neutral solvents, except ether, from which it crystallises unchanged; it resembles its isomeride very closely in appearance and in properties, but differs from it as regards melting point.

The *diaceiyl* derivative, $C_{12}H_{12}N_2O_4$, is formed when either of the glyoximes described above is treated with acetic anhydride at 0°, but a slight difference in the behaviour of the two compounds, as regards

the rapidity of solution, is observed. It crystallises in well-defined, highly refractive prisms, melts at 92°, and is readily soluble in most ordinary organic solvents, except ether.

Phenylazoxazole (*phenylfurazan*), $\begin{matrix}CH:N\\ |\\ CPh:N\end{matrix}>O$, is formed when the diacetyl derivative is kept in contact with sodium carbonate until it is completely converted into an oil, and also, but only slowly and to a limited extent, when either of the glyoximes or the diacetyl derivative is distilled with steam; it is best prepared by precipitating an alkaline solution of the glyoxime with carbonic anhydride, and extracting the precipitate with chloroform (see below). It crystallises from dilute alcohol in needles, melts at 30° (36°?), is volatile with steam, and volatilises very readily at the ordinary temperature; it is insoluble in water and cold alkalis, but very readily soluble in ether, chloroform, and benzene, and it dissolves unchanged in concentrated sulphuric acid.

Phenyloximidoacetonitrile, NOH:CPh·CN, is formed when phenylazoxazole or the diacetyl derivative (m. p. 92°) is warmed with soda or sodium carbonate, and also when phenylglyoxime is boiled with sodium carbonate; when the glyoxime is boiled with soda, it is only very slowly converted into the nitrile. Phenyloximidoacetonitrile is also the principal product (50 per cent. of the theoretical) of the action of hydroxylamine on dibromacetophenone in alkaline solution, a fact which was overlooked by Strassmann and by Schramm. It crystallises in plates, melts at 128°, dissolves freely in hot water and in the ordinary organic solvents, and is not volatile with steam; it is not hydrolysed by boiling, concentrated hydrochloric acid, and when heated with concentrated soda, it is only very slowly converted into phenyloximidoacetic acid, with evolution of ammonia. The *acetyl* derivative, NOAc:CPh·CN, prepared by boiling the nitrile, or either of the glyoximes, with acetic anhydride, separates from dilute alcohol in well-defined, rhombic crystals, melts at 68°, dissolves freely in all ordinary solvents, and is decomposed by soda, yielding the nitrile.

The following observations point to the existence of a third glyoxime, which is probably *phenylsynglyoxime*, $\begin{matrix}Ph\cdot C\text{———}C\cdot H\\ \|\quad\quad\quad\quad\|\\ N\cdot OH\quad OH\cdot N\end{matrix}$.

When either of the glyoximes described above is dissolved in soda, and carbonic anhydride passed through the solution cooled to −10°, a precipitate, containing about 33—36 per cent. of the theoretical quantity of phenylazoxazole, is produced; after extracting this compound by shaking with chloroform, there remains undissolved a substance which melts at 148—154°; this, on being dissolved in a very small quantity of acetic anhydride, yields an oily product. When this oil is distilled with water, it yields in the first few minutes a far larger quantity (above 51 per cent. of the theoretical) of phenylazoxazole than is obtained in the same time from either of the glyoximes, or from the acetyl derivative (m. p. 92°) described above, and then the rate of formation of this compound quickly diminishes; this oil is also very quickly converted into phenylazoxazole on treatment with cold soda, whereas the diacetyl derivative yields phenyloximidoaceto-

nitrile under the same conditions. These facts seem to show that the precipitate produced with carbonic anhydride consists principally of phenylazoxazole, and contains, in addition, a phenylglyoxime which differs from the other two compounds in properties, and probably has the configuration given above.

No evidence of the existence of the fourth theoretically possible isomeride was obtained. F. S. K.

Action of Nitrous Acid on Benzenylamidethoxime. By F. Tiemann (*Ber.*, **24**, 3453—3458; compare Tiemann and Krüger, Abstr., 1884, 1325; 1885, 790).—The author finds that when sodium nitrite is added in molecular proportion to a solution of benzenylamidethoxime acidified with a mineral acid or a strong organic acid, the character of the product depends on the acid employed. Benzenylethoxime chloride (*loc. cit.*) is formed in the presence of hydrochloric acid.

Benzenylethoxime bromide, CPhBr:NOEt, is obtained by dissolving the amidethoxime (1 mol.) in hydrobromic acid (2 mols.), cooling, cautiously adding a solution of sodium nitrite (1 mol.), gently heating at 40° until the evolution of nitrogen ceases, extracting with ether, and, after evaporating the solvent, distilling in a partial vacuum; it is an oil, insoluble in water, but readily soluble in alcohol and ether, and boils at 150° (45 mm.).

Benzenylethoxime nitrite, NO_2·CPh:NOEt, is formed when a solution of the amidethoxime (1 mol.) in dilute sulphuric acid is treated with sodium nitrite (2 mols.) in the cold. It is an oil of little stability, which dissolves in hot alkalis with decomposition, and is quickly converted into benzoic acid and ethoxylamine by hydrochloric acid; when it is shaken with cold potassium hydroxide solution and carbonic anhydride passed through the solution, ethyl benzhydroxamate is formed.

Benzenylethoxime acetate, OAc·CPh:NOEt, is prepared by dissolving benzenylamidethoxime in concentrated acetic acid, adding sodium nitrite solution at the temperature of the room, carefully neutralising, and extracting with ether; it is an oil which does not solidify decomposes into phenyl isocyanate on distillation, undergoes partial decomposition on boiling with water, and is readily soluble in alcohol and ether; when carefully warmed with a solution of potassium hydroxide in dilute alcohol, the potassium derivative of ethyl benzhydroxamate is obtained. A. R. L.

Dyeing with Aniline-black in the Dry Way. By S. Grawitz (*Compt. rend.*, **113**, 746—747).—It is well known that dyeing with aniline-black in the dry way seriously weakens the fibre, and that this result cannot be avoided by using a neutral salt of aniline.

According to Nietzki, aniline-black is a monobasic tetramine, and, if this be so, its formation will be represented by the equation $4C_6H_7N,HCl + 4O = C_{24}H_{29}N_4,HCl + 3HCl + 4H_2O$. The hydrogen chloride liberated in contact with the dry cellulose converts it into hydrocellulose and weakens the fibre. The remedy lies in adding acetates, or other organic salts of the alkalis or alkaline earths, to

the mixture for producing the black. Koechlin has stated that the presence of acetates prevents the formation of the black, but the author finds that this is not the case when the quantity of acetate added contains less than one equivalent of base for each equivalent of acid present in the form of aniline salt. Half an equivalent gives comparatively little protection, but the maximum benefit is obtained with a quantity of acetate equivalent to three-fourths of the aniline salt present, a result which supports Nietzki's view, according to which three-fourths of the acid in the aniline salt is liberated in the process of oxidation. C. H. B.

Thiophenylcarbamides. By S. Paschkowezky (*Ber.*, **24**, 3492).—The author has received a private communication from Bernthsen, in which he points out that the differences in the melting points recorded for thiodiphenylcarbamide chloride and dithiotetraphenylcarbamide by Paschkowezky (this vol., p. 164), and by Fränkel (Abstr., 1885, 1130), are due to the latter having neglected to correct the values he obtained. A. R. L.

Action of Potassium Cyanide on Halogen Derivatives of Ketones. By A. Obrégia (*Annalen*, **266**, 324—358).—The potassium derivative of cyanacetophenone is formed, with evolution of hydrogen cyanide, when bromacetophenone (1 mol.) is treated with potassium cyanide (2 mols.) in dilute alcoholic solution; after evaporating the alcohol and taking up the residue with water, the filtered solution is acidified, and the precipitated cyanacetophenone recrystallised from boiling water. The yield of pure cyanacetophenone (m. p. 80—81°) is 64 per cent. of the theoretical; its aqueous solution has an acid reaction. The *sodium* derivative crystallises in small, nacreous plates, is readily soluble in alcohol, and is only slowly decomposed by carbonic anhydride; the ammonium derivative is unstable; on treating a solution of the sodium derivative with metallic salts, the corresponding metallic derivatives are precipitated. The *hydrazone* separates from alcohol in almost colourless crystals, melts at 134—135° with previous softening, and is very readily soluble in ether and chloroform, but only moderately easily in cold alcohol, and insoluble in cold water.

A compound of the composition $C_9H_8N_2O$ is formed when an alkaline solution of cyanacetophenone is treated with hydroxylamine at the ordinary temperature; it crystallises in colourless, lustrous, rectangular plates or short needles, melts at 110—112°, and is readily soluble in chloroform, alcohol, benzene, ether, and acetone, but almost insoluble in light petroleum, cold alkalis, and concentrated ammonia; it has a neutral reaction, and crystallises unchanged from hot soda. The *hydrochloride* melts at 98—100°; the *sulphate* decomposes at 169—173°, and is resolved into its components by cold water. When boiled with dilute acids, it yields cyanacetophenone and phenylisoxazolone; the last-named compound is also formed when an alcoholic solution of cyanacetophenone and hydroxylamine hydrochloride is kept for a long time. It will be seen that the compound just described does not show all the properties of a true oxime; its constitution is probably represented by the formula $\begin{matrix}CH_2\cdot CO\\ |\\ CPh:N\end{matrix}>NH$.

Benzoylacetamide, $CH_2Bz{\cdot}CO{\cdot}NH_2$, is obtained when cyanacetophenone is treated with concentrated sulphuric acid at the ordinary temperature, and, after keeping for about 48 hours, the product precipitated with ice; it crystallises from hot water in lustrous needles or prisms, melts at 111—113°, and is almost insoluble in light petroleum, and only moderately easily soluble in benzene and ether, but readily in alcohol, chloroform, acetone, alkalis, and ammonia; it has a neutral reaction, and its solutions give an intense violet coloration with ferric chloride. It is decomposed by boiling alkalis with formation of ammonia, acetic acid, and benzoic acid, and when heated alone or with water, it yields carbonic anhydride and acetophenone. The *hydrazone* crystallises from dilute alcohol in yellowish needles, melts at 128—130°, and is soluble in ether. When benzoylacetamide is treated with hydroxylamine hydrochloride in alcoholic or ammoniacal solution, it is converted in phenylisoxazolone.

The crystalline compound (m. p. 179—180°) obtained by treating chloracetone with potassium cyanide in aqueous solution (compare Hantzsch, Abstr., 1890, 1094) has the molecular formula $C_8H_{10}N_2O_2$, as was proved by molecular weight determinations, by Raoult's method, in glacial acetic acid solution, and its constitution is probably that of a *β-methylhydroxy-γ-cyanacetobutyronitrile*,

$$CN{\cdot}CHAc{\cdot}CMe(OH){\cdot}CH_2{\cdot}CN.$$

Hydroxyhydrocyanomesitenelactone, $CN{\cdot}C\lessdot^{CMe(OH){\cdot}CH_2}_{CMe—O—CO}$, the *nitrile* of *hydroxyhydroisodehydracetic acid*, is obtained when the crystalline compound (m. p. 179—180) just mentioned is dissolved in very dilute sulphuric acid; it crystallises from hot water in colourless, lustrous needles, melts at 65°, and is very readily soluble in alcohol, chloroform, benzene, acetone, and boiling water, but only moderately easily in ether, and almost insoluble in light petroleum. Its aqueous solution gives, with ferric chloride, first a brownish, and then a violet, coloration; the freshly prepared solution in dilute alcohol has only a very feebly acid reaction, but after keeping for some time the acidity increases very considerably. It dissolves unchanged in cold, concentrated acids, and also in alkalis, ammonia, and alkali carbonates. The *bromo*-derivative, $C_8H_6BrNO_3$, can be prepared by treating the lactone or the crystalline compound (m. p. 179—180°) with bromine in alcoholic solution; it crystallises from dilute alcohol in slender, lustrous needles, melts at 98—100°, and is readily soluble in benzene, chloroform, ether, alcohol, and boiling water; its aqueous solution has an acid reaction, and only gives a slight violet coloration with ferric chloride after having been boiled.

β-Hydroxy-γ-acetoisovaleric acid, $CH_2Ac{\cdot}CMe(OH){\cdot}CH_2{\cdot}COOH$, is formed, with liberation of carbonic anhydride, when the lactone is boiled with barium hydroxide until the evolution of ammonia is at an end; it is a thick, yellow, odourless liquid, readily soluble in water, alcohol, and ether. The *phenylhydrazone* is an oil; the *paratolylhydrazone* is a yellowish, very unstable substance, and decomposes at 81—85°. The *barium* salt is a yellowish, amorphous powder, readily soluble in water and alcohol; it seems to have the composition

$(C_7H_{11}O_4)_2Ba + C_7H_{10}O_4Ba$. The *silver* salt, $2C_7H_{11}O_4Ag + C_7H_{10}O_4Ag_2 + H_2O$, is very unstable, and very readily soluble in cold water. The *copper* salt is a green, vitreous, hygroscopic substance.

A compound of the composition $C_8H_{13}N_3O_4 + 3H_2O$ is obtained when hydroxyhydrocyanomesitenelactone is treated with hydroxylamine in very dilute alkaline solution, and the precipitate recrystallised from boiling water, from which it separates in colourless, lustrous needles; it slowly loses the whole of its water over sulphuric acid, the anhydrous crystals decomposing at 184—185°. It is very sparingly soluble in ether, acetone, light petroleum, and cold water, but more readily in alcohol, chloroform, benzene, and boiling water; its aqueous solution has a pronounced acid reaction, and gives, with ferric chloride, a brownish-violet coloration. This compound is probably the lactam of β-methylhydroxy-γ-acetoxime-δ-isonitrosoamidovaleric acid, and its constitution may be represented by the formula

$$NOH{:}CMe{\cdot}CH{<}\begin{matrix}C(NOH)—NH\\CMe(OH){\cdot}CH_2\end{matrix}{>}CO.$$

F. S. K.

Action of Ammonia and Aniline on Halogen-substituted Nitrobenzoic Acids. By A. Grohmann (*Ber.*, **24**, 3808—3815).—In a previous communication (Abstr., 1891, 305), the author has shown that the halogen in the ethyl salt, amide, and anilide of 4 : 3-bromonitrobenzoic acid may be readily replaced by the amido- and anilido-groups; in the present paper he describes similar experiments made with 2 : 5-bromonitrobenzoic acid.

2 : 5-*Bromonitrobenzoic chloride*, $NO_2{\cdot}C_6H_3Br{\cdot}COCl$, is readily obtained by the action of phosphorus pentachloride on the acid, and crystallises from alcohol in greyish crystals melting at 63°. The *amide*, $NO_2{\cdot}C_6H_3Br{\cdot}CONH_2$, is prepared from the chloride by warming with ammonium carbonate on the water-bath, and crystallises from alcohol in white, lustrous needles which melt at 197—198°; the *anilide*, $NO_2{\cdot}C_6H_3Br{\cdot}CO{\cdot}NHPh$, obtained by gently warming the chloride with aniline, forms yellowish-white, acicular crystals, and melts at 166°; both compounds are soluble in alcohol and acetone, and insoluble in water and benzene.

When ethyl 2 : 5-bromonitrobenzoate is heated in a sealed tube with alcoholic ammonia, it is converted into *ethyl* 2 : 5-*amidonitrobenzoate*, $NO_2{\cdot}C_6H_3(NH_2){\cdot}COOEt$, which crystallises from alcohol in pale-yellow needles melting at 148°. If aniline be substituted for ammonia, the corresponding *ethyl* 2 : 5-*anilidonitrobenzoate* is obtained; it separates from alcohol in small, yellow plates, and melts at 118°. The amide and anilide above described also readily react with ammonia and aniline respectively, forming the corresponding amido- and anilido-compounds. 2 : 5-*Amidonitrobenzamide*,

$$NO_2{\cdot}C_6H_3(NH_2){\cdot}CONH_2,$$

crystallises in orange-yellow needles, and melts at 230°; 2 : 5-*anilidonitrobenzanilide*, $NO_2{\cdot}C_6H_3(NHPh){\cdot}CO{\cdot}NHPh$, separates from alcohol in tufts of very slender, yellow needles, resembling silk fibres, and melts at 159°.

2 : 4-*Chloronitrobenzoic chloride* is prepared from the acid in the

usual manner, and is a yellowish-brown substance melting at 115°. It is converted by ammonium carbonate and aniline respectively into the *amide* and *anilide;* the former crystallises from alcohol in grey scales, and melts at 172°, whilst the latter is a white, amorphous substance melting at 168°. In these compounds, unlike the 4 : 3- and 2 : 5-compounds, the halogen cannot be displaced by further heating with ammonia or aniline. The same is also true of 4 : 2-*chloronitrobenzoic acid*, which was prepared by displacing the amido-group in 4 : 2-amidonitrotoluene by chlorine and oxidising the chloronitrotoluene thus obtained.

From these results, it appears that when the nitro- and carboxyl-groups are simultaneously in the ortho- and para-position relatively to the halogen, the latter may be readily displaced, but that this is no longer possible when one of these groups takes up the meta-position.

To his previous communication on 4 : 3-bromonitrobenzoic acid (*loc. cit.*), the author adds that this acid is converted by alcoholic ammonia at 170° into the 4 : 3-amidonitrobenzoic acid described by Griess (*Ber.*, **5**, 855) and Salkowski (*Annalen*, **173**, 53).

H. G. C.

Oximes of some Ketonic Acids. By F. Garelli (*Gazzetta*, **21**, ii, 173—188).—In a previous memoir (Abstr., 1891, 711), the author reported his inability to prepare the oximido-compounds of dioxymethylenephenylglyoxylic acid, apionylglyoxylic acid, and paramethoxyglyoxylic acid; he has, however, since succeeded in preparing them, and finds them to be very unstable, readily losing the elements of water and carbonic anhydride, and yielding the corresponding nitriles.

Methyl dioxymethylenephenylglyoxylate, $CH_2<^{O}_{O}>C_6H_3\cdot CO\cdot COOMe$, is prepared by saturating a solution of dioxymethylenephenylglyoxylic acid in methyl alcohol with dry hydrogen chloride. The alcohol is distilled off and water added; the salt separates as an oil which soon solidifies, and is crystallised from dilute alcohol. Small colourless needles, melting at 66°, soluble in alcohol and ether, and almost insoluble in water, are thus obtained. The alcoholic solution of this ethereal salt is treated with a slight excess of hydroxylamine hydrochloride and heated in a reflux apparatus on the water-bath for two hours. The alcohol is distilled off, the residual oil dissolved in dilute potash, filtered from a small quantity of piperonylnitrile, and the solution saturated with carbonic anhydride; *methyl dioxymethylenephenyloximidoacetate* is then thrown down, and on reprecipitation from its solution in benzene, by the addition of light petroleum, is obtained in tufts of small crystals melting without decomposition at 102°. This substance is soluble in water and alcohol, and on hydrolysis with dilute potash at a temperature below 60°, yields *dioxymethylenephenyloximidoacetic acid*

$$CH_2<^{O}_{O}>C_6H_3\cdot C(NOH)^{\beta}\cdot COOH,$$

as a whiteish mass; on precipitation from its acetic solution by light

petroleum, it may be obtained in minute crystals, soluble in sodium carbonate solution, alcohol, ether, benzene, and water. It melts with decomposition at 150—151°, and its aqueous solution gives white precipitates with lead and mercury salts and a green precipitate with copper acetate in concentrated solutions. This acid may also be prepared by heating a dilute solution of dioxymethylenephenylglyoxylic acid at 60—70° with the calculated quantity of hydroxylamine hydrochloride. It is readily converted into piperonylonitrile by passing a current of dry hydrogen chloride into its ethereal solution; the conversion also proceeds spontaneously in dilute aqueous solutions, and is hastened by the presence of acids or of hydroxylamine hydrochloride. The *acetyl* derivative is obtained on heating it with a slight excess of acetic chloride; on cooling, colourless, rectangular prisms separate, melting with decomposition at 139—140°. When hydrolysed at 0° with dilute potash and extracted with ether, the oxime is regenerated; at higher temperatures, the nitrile is the principal product of the action.

Compounds analogous to those of dioxymethylenephenylglyoxylic acid may be prepared from apionylglyoxylic acid by the same methods. *Methyl apionylglyoxylate*, $CH_2<^{O}_{O}>C_6H(OMe)_2\cdot CO\cdot COOMe$, crystallises from dilute alcohol in needles melting at 62°; it is very soluble in alcohol and ether, sparingly in benzene, and insoluble in water. Its *oxime*, $CH_2<^{O}_{O}>C_6H(OMe)_2\cdot C(NOH)^{\beta}\cdot COOMe$, is obtained in minute, colourless crystals melting at 129° without decomposition; on hydrolysis, it yields *apionyloximidoacetic acid* in splendid, white scales, very soluble in alcohol, sparingly in boiling water, less so in benzene, and insoluble in ether. Its aqueous solution gives no precipitate with salts of lead, copper, or mercury. No acetyl derivative could be prepared.

Paramethoxyphenyloximidoacetic acid, $OMe\cdot C_6H_4\cdot C(NOH)^{\beta}\cdot COOH$, is prepared from paramethoxyphenylglyoxylic acid in the manner indicated above, and separates from ethyl acetate in large, colourless crystals, very soluble in water, alcohol, and ether; it melts at 145—146° with complete decomposition. The α-oximido-acid cannot be prepared by carrying out the reaction at 0°. On heating with acetic anhydride or acetic chloride, a small quantity of an *acetyl* derivative is obtained. It melts with complete decomposition at 118°, is decomposed with formation of anisonitrile by cold solutions of the alkali carbonates, and on hydrolysis at 0°, yields only the original β-oximido-acid.

Ciamician and Silber (Abstr., 1890, 965) found that isosafrole yielded piperonylic acid and dioxymethylenephenylglyoxylic acid on oxidation with permanganate, the author finds that a small quantity of dioxymethylenephenylglycollic acid is also produced (30 grams of isosafrole yield 0·5 gram of the acid). This acid is separated by means of its solubility in water, and melts at 156°, not at 152—153°, as found by Lorenz (Abstr., 1881, 727).

The ketonic acids obtained from safrole, anethoïl, methyleugenol, and apiole, when dissolved in benzene and treated with thiophen in

concentrated sulphuric acid solution, impart an intense red coloration to the thiophen, the benzene solution remaining colourless; on dilution, the solution becomes successively violet and dirty green. The solutions of these acids in phenol, when heated with concentrated sulphuric acid on the water-bath, soon turn blue; gas is then abundantly evolved and the solution becomes red; on pouring the product into water, the colouring matter separates as a flocculent precipitate insoluble in water, but readily soluble in soda, and in solutions of the alkali carbonates. A green colouring matter is produced on heating the acids with dimethylaniline and zinc chloride.

W. J. P.

Derivatives of Mesitylene. By E. Feith (*Ber.*, **24**, 3542—3545; compare Claus, Abstr., 1890, 979, and Dittrich and Meyer, Abstr., 1891, 1224).—The air-dried barium salt of mesitylglyoxylic acid contains 3 mols. H_2O, of which it loses two over sulphuric acid. The *zinc* salt, with $4H_2O$, crystallises in lustrous plates and loses 3 mols. H_2O over sulphuric acid. The *methyl* salt, $C_{12}H_{14}O_3$, boils at about 170° under a pressure of 100 mm. When mesitylglyoxylic acid is heated, it is decomposed into trimethylbenzaldehyde and trimethylbenzoic acid, the *methyl* salt of which crystallises in colourless plates melting at 139—140°.

Trimethylbenzaldehyde, $C_6H_2Me_3{\cdot}CHO$, is an oil, boils at 235—240°, and gradually oxidises on exposure to the air; its *oxime*,

$$C_6H_2Me_3{\cdot}CH{:}NOH,$$

crystallises in small needles, melts at 127°, and dissolves freely in alcohol, ether, and alkalis; its *hydrazone*, $C_6H_2Me_3{\cdot}CH{:}N_2HPh$, separates from dilute alcohol in colourless crystals, and is very unstable.

Mesitylglycollic acid, $C_6H_2Me_3{\cdot}CH(OH){\cdot}COOH$, prepared by reducing mesitylglyoxylic acid with sodium amalgam in alkaline solution, crystallises from water in large, well-defined, transparent plates, melts at 147°, and is readily soluble in alcohol and ether, but only sparingly in cold water. The *silver* salt, $C_{11}H_{13}O_3Ag$, is amorphous. The *methyl* salt, $C_{12}H_{16}O_3$, prepared from the silver salt, separates from light petroleum in colourless, nodular crystals, and melts at 92°. The *chloralide*, $C_6H_2Me_3{\cdot}CH<\begin{matrix}O\text{——}\\CO{\cdot}O\end{matrix}>CH{\cdot}CCl_3$, is formed when the acid is heated at 120—130° for two days with anhydrous chloral; it crystallises from light petroleum in well-defined plates, melts at 125°, and is readily soluble in benzene, chloroform, and ether, but more sparingly in alcohol.

F. S. K.

Thiocoumarin and its Analogues. By F. Aldringen (*Ber.*, **24**, 3459—3466).—Tiemann has shown (Abstr., 1886, 880) that thiocoumarin is formed when coumarin is fused with phosphorus pentasulphide. The object of the present work was to examine the behaviour of certain homologues of coumarin and of some other δ-lactones.

α-Methylthiocoumarin, $C_6H_4<\begin{matrix}CH{:}CMe\\|\\O\text{—}CS\end{matrix}$, is prepared by heating

α-methyl-coumarin (m. p. 90°) with phosphorus pentasulphide, boiling the melt with benzene, crystallising from absolute alcohol, and washing the crystals with carbon bisulphide; it forms yellow needles, melts at 122°, sublimes without decomposition, and is insoluble in water and light petroleum, but readily soluble in alcohol, ether, and benzene; it yields α-methylcoumarin on boiling with alcoholic potash.

α-Methylcoumaroxime, $C_6H_4<\begin{matrix}CH:CMe\\ |\\ O—C:NOH\end{matrix}$, is formed when the α-methylthiocoumarin is boiled with hydroxylamine in alcoholic solution; it crystallises from water or dilute alcohol in colourless needles, and melts at 166°. Ferric chloride does not give a coloration as with coumaroxime (see Tiemann, *loc. cit.*), and the same is true of the homologous compounds to be described; they are also without action on Fehling's solution. It dissolves in alkalis and acids, is stable towards the former, but yields α-methylcoumarin when boiled with concentrated hydrochloric acid; the *acetyl derivative*,

$$C_6H_4<\begin{matrix}CH:CMe\\ |\\ O—N\cdot OAc,\end{matrix}$$

obtained by dissolving the oxime in an excess of warm acetic chloride, melts at 56°. The *hydrazone*, $C_6H_4<\begin{matrix}CH:CMe\\ |\\ O—C:N_2HPh,\end{matrix}$ is produced by boiling α-methylthiocoumarin with phenylhydrazine in alcoholic solution for about a week; it crystallises from alcohol in yellow needles, melts at 116°, is insoluble in water, and dissolves in concentrated sulphuric acid with an intense green colour.

The following derivatives of α-ethylcoumarin (m. p. 71°) were prepared in a similar manner to the methyl compounds:—*α-Ethylthiocoumarin* forms small, yellowish-red plates, and melts at 93—94°; *α-ethylcoumaroxime* crystallises in long, white needles, melts at 157°, and yields an *acetyl derivative* melting at 61°; whilst *α-ethylcoumarophenylhydrazone* melts at 115°.

Derivatives of α-Isopropylcoumarin (m. p. 54°).—*α-Isopropylthiocoumarin* forms reddish-yellow needles, and melts at 81°; *α-isopropylthiocoumaroxime* crystallises in white prisms, melts at 171°, and yields an *acetyl derivative* melting at 85°; whilst *α-isopropylcoumarophenylhydrazone* melts at 112°.

Derivatives of Methylumbelliferone (m. p. 114°).—Umbelliferone is not readily converted into the thio-derivative by fusion with phosphorus pentasulphide, whereas the methyl derivative exhibits the same behaviour as coumarin.

Methylthioumbelliferone, $OMe\cdot C_6H_2<\begin{matrix}CH:CH\\ |\\ O—CS\end{matrix}$ (OMe at 4; CH:CH at 1; O—CS at 2), forms yellow needles, melts at 114°, and dissolves in boiling alkalis with decomposition. *Methylumbelliferonoxime* crystallises from water in long, felted needles, melts at 138°, and gives a brownish-red colour with ferric chloride. *Methylumbelliferonephenylhydrazone* is obtained by boiling for a fortnight a mixture of methylthioumbelliferone with phenylhydrazine in molecular proportion, dissolved in alcohol; it crystallises

from alcohol in thick, yellow needles, melts at 115°, and dissolves in concentrated sulphuric with a bluish-green colour. A. R. L.

Action of Ammonia and Aniline on Negatively-substituted Halogen-benzenesulphonic Acids. By P. Fischer (*Ber.*, **24**, 3785—3808).—It was found that in the case of the two chloronitrobenzenesulphonic acids $NO_2 \cdot C_6H_3Cl \cdot SO_3H$ [$Cl : NO_2 : SO_3H = 1 : 2 : 4$ and $1 : 4 : 2$ respectively], the two bromosulphobenzoic acids

$COOH \cdot C_6H_3Br \cdot SO_3H$ [$Br : COOH : SO_3H = 1 : 2 : 4$ and $1 : 4 : 2$ respectively], and bromobenzenedisulphonic acid, $C_6H_3Br(SO_3H)_2$ [$Br : (SO_3H)_2 = 1 : 2 : 4$], the action of ammonia or aniline is to displace the halogen by the amido- or anilido-group. In all of these acids a para- and an ortho-position, relatively to the halogen atom, are occupied by negative groups.

Metanitroparamidobenzenesulphonic acid, $NH_2 \cdot C_6H_3(NO_2) \cdot SO_3H$ [$1 : 2 : 4$], is obtained as the ammonium salt by heating metanitroparachlorobenzenesulphonic acid with alcoholic ammonia at 120—140°. The *barium salt*, $(C_6H_5N_2SO_5)_2Ba + 2\frac{1}{2}H_2O$, forms yellow crystals; the acid itself forms an amorphous, yellow precipitate. When heated with concentrated hydrochloric acid at 150°, the sulphonic group is removed, and orthonitraniline is formed; this proves that the NO_2 group and the chlorine atom in the original nitrochlorosulphonic acid occupy the ortho-positions relatively to each other. *Paramidometanitrobenzenesulphonamide*, $NH_2 \cdot C_6H_3(NO_2) \cdot SO_2 \cdot NH_2$ [$1 : 2 : 4$], is obtained by heating parachlorometanitrobenzenesulphonamide with alcoholic ammonia at 120°. It crystallises from alcohol or water in deep yellow needles or lustrous, golden plates, melts at 206—207°, and is such a feeble base that it forms no salts with acids.

Metanitro-orthamidobenzenesulphonic acid [$NH_2 : NO_2 : SO_3H = 1 : 4 : 2$] was obtained in the same way as the isomeric acid. The barium salt, $(C_6H_5N_2SO_5)_2Ba + H_2O$, forms yellow crystals. The acid itself crystallises from water in small, yellow crystals, and yields paraphenylenediaminesulphonic acid, $C_6H_3(NH_2)_2 \cdot SO_3H$, on reduction by Claisen's method. Its *sulphonamide* forms yellow needles or plates melting at 210°.

With parachlorometanitrobenzenesulphonic acid, aniline yields an *aniline salt*, $NO_2 \cdot C_6H_3Cl \cdot SO_3 \cdot NH_3Ph$ [$= 2 : 1 : 4$], in lustrous, white crystals. This, when heated with excess of aniline, yields the *aniline salt* of *metanitroparanilidobenzenesulphonic acid*,

$$NO_2 \cdot C_6H_3(NHPh) \cdot SO_3 \cdot NH_3Ph \ [= 2 : 1 : 4],$$

which forms large groups of yellowish-brown needles, and dissolves in alcohol, acetic acid, acetone, and hot water, but not in ether or benzene. The *barium salt*, $(C_{12}H_9N_2SO_5)_2Ba + H_2O$, forms lustrous, dark golden plates. The acid forms orange-coloured crystals, decomposing at 200° without melting, and dissolves readily in water, alcohol, acetic acid, and acetone, but not in benzene and ether. The *alkali salts*, $C_{12}H_9N_2SO_5Na + H_2O$, &c., are orange-yellow, but at 110° lose water and become brick-red; the anhydrous salts, however, take up water from the air, becoming again orange-yellow. The *ammonium salt*,

$$C_{12}H_9N_2SO_5 \cdot NH_4 + \tfrac{1}{2}H_2O,$$

forms lustrous, yellow plates. By the action of phosphorus pentachloride on the acid, the *sulphochloride* is obtained; it crystallises from ether in yellowish-brown needles, and with ammonium carbonate yields the *sulphonamide*, as lustrous, red crystals melting at 162°. The *sulphanilide* is best obtained by the action of aniline on the chloronitrobenzenesulphonic chloride; it forms long, orange-yellow needles, melts at 157°, and dissolves readily in alcohol, acetone, and acetic acid.

Paranilidometamidobenzenesulphonic acid, $NHPh\cdot C_6H_3(NH_2)\cdot SO_3H$ [=1 : 2 : 4], is prepared by reducing the barium salt of the corresponding anilidonitro-acid by Claisen's method; it forms a crystalline precipitate, which darkens in the air and gives a violet-red colour with ferric chloride. The *barium salt*, $(C_{12}H_{11}N_2SO_6)_2Ba + 2H_2O$, forms tiny, brownish needles. The *sulphanilide*, prepared by reducing the corresponding nitrosulphanilide with alcoholic ammonium sulphide, forms colourless, lustrous needles melting at 157°, and giving a deep violet colour with concentrated sulphuric acid. The *hydrochloride* forms white needles melting at 181—182° with decomposition. Metanitroparanilidobenzenesulphonic acid yields orthodinitrodiphenylamine when heated at 130—140° with concentrated hydrochloric acid. By adding potassium nitrite to an acetic acid solution of this base, *orthonitrodiphenylnitrosamine*, $NO_2\cdot C_6H_4\cdot NPh\cdot NO$, is obtained. It forms nearly colourless plates melting at 99—100°; it does not give Liebermann's nitrosamine reaction with phenol and sulphuric acid, but yields a deep violet, and not a deep blue, colour.

Orthochlorometanitrobenzenesulphonic acid yields, with aniline, the *aniline salt*, which forms long, lustrous, white needles, decomposing above 200° without melting. When heated with aniline, this yields *metanitro-orthanilidobenzenesulphonic acid*, as the *aniline salt*, in large, brown needles with a violet lustre; it dissolves in water, alcohol, and acetone, but not in ether or benzene. The *barium salt*,

$$(C_{12}H_9N_2SO_5)_2Ba + 5H_2O,$$

forms lustrous, orange needles. The *acid* itself crystallises in small, lustrous, olive-green plates. The *potassium salt* forms anhydrous, orange needles, and with phosphorus pentachloride yields the *sulphonic chloride*, as greenish-yellow needles melting at 102—104° and readily soluble in ether, benzene, and chloroform. With ammonium carbonate, it yields the *sulphonamide*, which separates from alcohol in reddish-yellow crystals melting at 173°, and insoluble in water. The *sulphanilide* was obtained from aniline and the chloronitrosulphonic chloride; it crystallises from alcohol in lustrous, greenish-yellow needles melting at 164°. *Orthanilidometamidobenzenesulphonic acid*, $NHPh\cdot C_6H_3(NH_2)\cdot SO_3H$ [= 1 : 4 : 2], is obtained as the *barium salt*, $(C_{12}H_{11}N_2SO_3)_2Ba + H_2O$ (lustrous, silver-grey plates), by reducing the barium salt of the corresponding nitro-acid by Claisen's method. It yields highly-coloured oxidation products; for example, with ferric chloride, it gives a red colour passing into violet. The acid forms dark-coloured plates. The *sulphanilide*, obtained by reducing the corresponding nitrosulphanilide with alcoholic ammonium sulphide at 120—130°, forms lustrous plates melting at 171°, and gives a violet colour with strong sulphuric acid. Its *hydrochloride* blackens at 200°,

and melts with decomposition at 215°, and gives an olive-green colour with ferric chloride.

Paramidometasulphobenzoic acid,

$$NH_2{\cdot}C_6H_3(SO_3H){\cdot}COOH\ [1:2:4],$$

is obtained as the diammonium salt by heating the corresponding bromosulphobenzoic acid with alcoholic ammonia at 160- -180°. The *barium salt*, $C_7H_5NSO_5Ba + 2H_2O$, forms large, colourless crystals, the *potassium salt* anhydrous, transparent needles. The acid itself crystallises from water in slender needles. Parabromometasulphobenzoic acid yields with aniline the *aniline salt*, which crystallises from water in long, lustrous, white needles, decomposing above 200° without melting, and when heated with aniline yields the *aniline salt* of *paranilidometasulphobenzoic acid*, $NHPh{\cdot}C_6H_3(SO_3H){\cdot}COO{\cdot}NH_3Ph$. The *barium salt*, $C_{13}H_9NSO_5Ba + 3\frac{1}{2}H_2O$, with sulphuric acid, yields the free acid as small, lustrous, nearly colourless plates.

Orthobromometasulphobenzoic acid, $SO_3H{\cdot}C_6H_3Br{\cdot}COOH\ [4:1:2]$, was prepared by treating orthobromobenzoic acid (obtained by oxidising orthobromotoluene) with fuming sulphuric acid. When heated with alcoholic ammonia at 160—180°, it yields the ammonium salt of the *amido-acid*. The *barium salt*, $C_7H_5NSO_5Ba + 2\frac{1}{2}H_2O$, forms colourless crystals. With aniline, the bromo-acid yields an *aniline salt*, and this, when heated with aniline in glycerol solution, yields the *aniline salt* of *orthanilidometasulphobenzoic acid*,

$$NHPh{\cdot}C_6H_3(SO_3H){\cdot}COO{\cdot}NH_3Ph\ [1:4:2],$$

in brownish plates. The *barium salt*, $C_{13}H_9NSO_5Ba + 5H_2O$, forms lustrous, yellowish plates. The acid crystallises from water in fine needles which decompose without melting.

Amidobenzenemetadisulphonic acid (*disulphanilic acid*),

$$NH_2{\cdot}C_6H_3(SO_3H)_2\ [1:2:4],$$

was obtained as the neutral ammonium salt by heating the corresponding bromodisulphonic acid with alcoholic ammonia at 160—180°. The *amidodisulphonamide*, $NH_2{\cdot}C_6H_3(SO_2{\cdot}NH_2)_2\ [1:2:4]$, was obtained from ammonia and the bromodisulphonamide. It crystallises from water in lustrous, white plates melting at 235°. The bromodisulphonic acid yields with aniline the *dianiline salt*, which forms transparent, colourless plates soluble in water and glycerol, but not in alcohol. When heated with aniline in glycerol solution, it yields *anilidobenzenemetadisulphonic acid* (*diphenylamineorthoparadisulphonic acid*), which is very soluble in water, and could not be obtained crystalline. The *barium salt*, $C_{12}H_9NS_2O_6Ba + 3H_2O$, is a yellowish, amorphous substance. The *disulphanilide* is best obtained by heating the corresponding bromobenzenedisulphonic chloride with aniline. It forms large, yellowish crystals melting at 221—222°, and dissolves readily in alcohol, less readily in acetic acid, sparingly in glycerol, and not at all in water. C. F. B.

Acetoximes. By H. Wege (*Ber.*, **24**, 3537—3540).—The acetyl and the isobutyl derivatives of acetoxime were prepared from the oxime by Hinsberg's method (Abstr., 1891, 49); they are both oils.

Acetoximephenylsulphone, $CMe_2{:}N{\cdot}O{\cdot}SO_2Ph$, is easily obtained by shaking a concentrated aqueous solution of acetoxime with soda and phenylsulphonic chloride; it crystallises from a mixture of ether and light petroleum in long, colourless needles, melts at 52·5°, and explodes at 128°, with formation of phenylsulphonic acid, ammonia, and small quantities of nitrogen.

Acetoximeparatolylsulphone, $CMe_2{:}N{\cdot}O{\cdot}SO_2{\cdot}C_6H_4Me$, prepared in like manner, crystallises from dilute alcohol in colourless scales, melts at 89°, and decomposes at 135° with a slight explosion. The corresponding *β-naphthyl* derivative, $C_{13}H_{13}NO_3S$, crystallises from alcohol in colourless or reddish plates melting at 87°.

When camphoroxime is shaken with soda and phenylsulphonic chloride, it seems to be converted into campholenonitrile. Benzophenoneoxime, under the same conditions, is converted into benzanilide; a similar intramolecular change also takes place when the chlorides of paratoluenesulphonic acid and naphthalenesulphonic acid are employed in the place of phenylsulphonic chloride.

F. S. K.

Action of Sulphonic Chlorides on Orthamidobenzamide. By E. Franke (*J. pr. Chem.* [2], **44**, 417—432; compare Abstr., 1887, 1043, 1044; 1890, 1289).—Benzenesulphoneorthamidobenzamide (Abstr., 1890, 1289) is insoluble in cold water and light petroleum, but dissolves in alcohol; it does not yield an anhydride when heated with water.

Ethyl benzenesulphoneorthamidobenzoate, $COOEt{\cdot}C_6H_4{\cdot}NH{\cdot}SO_2Ph$, obtained by the action of ethyl orthamidobenzoate (Abstr., 1885, 665) on benzenesulphonic chloride, crystallises from aqueous alcohol in white, quadratic prisms, melts at 92·5°, and dissolves easily in absolute alcohol, but not in water. When heated with aqueous ammonia at 140° for seven hours, or with alcoholic ammonia at 160° for 12 hours, it is converted into benzenesulphoneorthamidobenzamide; with alcoholic methylamine at 140°, it yields benzenesulphoneorthamidobenzomethylamide (see below).

The *potassium* and *silver* compounds of benzenesulphoneorthamidobenzamide are described, and the precipitates which the base gives with several of the salts of the heavy metals are detailed; the metals displace 1 atom of hydrogen from a molecule of the amide. The author retracts his former statements as to the obtaining of a hydrochloride and methyl derivative melting at 116° from benzenesulphoneorthamidobenzamide (Abstr., 1890, 1289).

The author did not succeed a second time in obtaining an anhydride by acting on benzenesulphoneorthamidobenzamide with phosphoric anhydride, or by dissolving it in dilute sodium hydroxide solution and precipitating by hydrochloric acid, or by heating it in alcohol at 210° (Abstr., 1890, 1289). *Anhydrobenzenesulphoneorthamidobenzamide*, $C_6H_4{<}\begin{matrix}CO{\cdot}NH\\ |\\ N:SOPh\end{matrix}$, is, however, readily obtained by heating a mixture of benzenesulphoneorthamidobenzamide and phosphoric chloride in molecular proportion, first at 60—70°, and finally at 175°; the mass is afterwards extracted with benzene, the solution precipitated

with water, and the compound recrystallised from dilute alcohol. It crystallises in pale yellow needles, melts at 145°, is very soluble in alcohol and hot benzene, less so in chloroform, ether, and water; it also dissolves in alkalis, and is precipitated unchanged by acids. When heated with concentrated hydrochloric acid, it is decomposed. Its *sodium*, *silver*, and *potassium* compounds were prepared.

Benzenesulphoneorthamidobenzomethylamide,

$$NHMe\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Ph,$$

is obtained as described above, or by heating anhydrobenzenesulphoneorthamidobenzamide with potassium hydroxide and methyl iodide in alcohol in a sealed tube at 120°, or by bringing together orthamidobenzomethylamide and benzenesulphonic chloride in molecular proportion. It crystallises from aqueous alcohol in white needles, melts at 114°, and is insoluble in cold water and light petroleum, but easily soluble in hot benzene, ether, and alcohol.

Benzenesulphoneorthomethamidobenzamide,

$$NH_2\cdot CO\cdot C_6H_4\cdot NMe\cdot SO_2Ph,$$

is prepared by heating molecular proportions of orthomethamidobenzamide (Abstr., 1887, 1044) and benzenesulphonic chloride together on the water-bath; the new compound is extracted from the product by very dilute alcohol, and recrystallised from hot benzene. It forms beautiful, rhombic laminæ, melts at 154° (uncorr.), and dissolves readily in warm alcohol and in warm, dilute alkalis; it is precipitated unchanged from the alkaline solutions on the addition of an acid.

Benzenesulphoneorthamidobenzophenylamide,

$$NHPh\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Ph,$$

prepared from benzenesulphonic chloride and orthamidobenzophenylamide, crystallises in needles which melt at 144—144·5°. *Benzenesulphoneorthamidobenzoylphenylhydrazine*, $N_2H_2Ph\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Ph$, was obtained by heating benzenesulphonic chloride and orthamidobenzoylphenylhydrazine together at 130—140°; the dirty-white needles which crystallised from water melted at 140—142°, but the yield was very small, and further investigation is needed.

Methylsulphoneorthamidobenzamide, $NH_2\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Me$, is obtained by the action of methylsulphonic chloride (b. p. 160—161°) on orthamidobenzamide; it crystallises from hot, dilute alcohol in almost white, very slender prisms, which melt at 156—157°; an anhydro-derivative could not be prepared.

When sulphuryl chloride and orthamidobenzamide react, dichloranthranilamide, $NH_2\cdot CO\cdot C_6H_2Cl_2\cdot NH_2$, is produced; this crystallises in dirty-yellow needles, and melts at 175—176°; on hydrolysis, it yields Dorsch's dichloranthranilic acid melting at 223—225° (Abstr., 1886, 360). Dorsch, however, gives the melting point of the amide corresponding with his acid as 284°. A. G. B.

Displacement of Halogen Atoms in the Benzene Ring. By M. Schöpff (*Ber.*, **24**, 3771—3784; compare Abstr., 1891, 304).—The general result of this research may be expressed thus:—If in

the benzene ring in which the halogen atom is contained there are also two negative groups, like or unlike, in the ortho- and para-positions relatively to this atom, then other groups, such as ·NH, ·NHR, and ·OH, can easily be substituted for the halogen; but if only one negative group is present, no such replacement occurs, except when this one group is ·NO_2. The negative groups may be ·NO_2, ·SO_3H, ·COOH, ·CO·R, or ·COH.

Parabromometanitrobenzophenone, $NO_2{\cdot}C_6H_3Br{\cdot}COPh$ [Br : NO_2 : CO = 4 : 3 : 1], is obtained by heating benzene with parabromometanitrobenzoic chloride in the presence of aluminium chloride. It forms white plates melting at 112—113°, and dissolves easily in benzene, acetone, chloroform, ether, and acetic acid, less easily in light petroleum. When heated with alcoholic ammonia at 130°, it yields *paramidometanitrobenzophenone*, $NH_2{\cdot}C_6H_3(NO_2){\cdot}COPh$, as small, yellow needles melting at 135°, and dissolving very readily in water. With alcoholic ethylamine, it yields *parethylamidometanitrobenzophenone*, $NHEt{\cdot}C_6H_3(NO_2){\cdot}COPh$, as yellow needles melting at 99—100°, and with aniline, *paranilidometanitrobenzophenone*,

$$NPHh{\cdot}C_6H_3(NO_2){\cdot}COPh,$$

as orange-coloured needles melting at 157°.

Diparabromometanitrobenzophenone,

$NO_2{\cdot}C_6H_3Br{\cdot}CO{\cdot}C_6H_4Br$ [Br : NO_2 : CO = 4 : 3 : 1 and CO : Br = 1 : 4],

is obtained by warming parabromometanitrobenzoic chloride and bromobenzene with aluminium chloride in carbon bisulphide. It forms needles melting at 118°, and has the same solubility as the monobromo-compound. With alcoholic ammonia at 130°, it yields *paramidometanitroparabromobenzophenone*, $NH_2{\cdot}C_6H_3(NO_2){\cdot}CO{\cdot}C_6H_4Br$, as a yellow substance melting at 171°. The corresponding *anilido-derivative*, $NHPh{\cdot}C_6H_3(NO_2){\cdot}CO{\cdot}C_6H_4Br$, forms yellow needles melting at 180°.

Diparabromodimetanitrobenzophenone,

$$CO(C_6H_3Br{\cdot}NO_2)_2 \text{ [Br : } (NO_2) : CO = 4 : 3 : 1],$$

is obtained by treating either diparabromobenzophenone or diparabrometanitrobenzophenone with fuming nitric acid. It forms needles melting at 152—153°. With aniline, it yields *diparanilidodimetanitrobenzophenone*, $CO[C_6H_3(NO_2){\cdot}NHPh]_2$, melting at 219°.

Orthobromometanitrobenzophenone, $NO_2{\cdot}C_6H_3Br{\cdot}COPh$, melting at 115°, was prepared in a similar manner to the isomeric parabromo-compound, and resembles the latter in its chemical behaviour; with aniline, it yields *orthanilidometanitrobenzophenone* in lemon-coloured needles melting at 135°.

Parabromometanitrobenzaldehyde, $NO_2{\cdot}C_6H_3Br{\cdot}CHO$ [Br : NO_2 : CO = 4 : 3 : 1] (the *aldoxime* of which, $NO_2{\cdot}C_6H_3Br{\cdot}CH{:}NOH$, forms yellow needles melting at 145—146°, and dissolves readily in alcohol, less readily in water), when boiled with aqueous soda, yields *parahydroxymetanitrobenzaldehyde*, $OH{\cdot}C_6H_3(NO_2){\cdot}CHO$, which crystallises from water in yellowish-brown needles melting at 139—140·5°. The *hydrazone*, $OH{\cdot}C_6H_3(NO_2){\cdot}CH{:}N_2HPh$, crystallises from alcohol in small,

dark-red needles melting at 175—176°. The aldehyde is identical with the substance obtained by nitrating parahydroxybenzaldehyde.

When asymmetrical bromoxylene, $C_6H_3Me_2Br$ [Br : Me_2 = 1 : 2 : 4], is boiled with aqueous potassium permanganate, it is oxidised to *asymmetrical bromisophthalic acid*, $C_6H_3Br(COOH)_2$, but a little asymmetrical hydroxyisophthalic acid, $OH{\cdot}C_6H_3(COOH)_2$, is also formed. To separate these, they are converted into their ethereal salts, of which that of the hydroxy-acid may be removed by dissolving it in dilute aqueous soda, which does not dissolve the other salt. *Asymmetrical ethyl bromisophthalate*, $C_6H_3Br(COOEt)_2$, is thus obtained pure; it is a colourless oil with an odour like that of rum; it boils at 320—325° under 365 mm. pressure, and, when treated with concentrated hydrochloric acid, yields *asymmetrical bromisophthalic acid*, $C_6H_3Br(COOH)_2$ [Br : $(COOH)_2$ = 1 : 2 : 4]. This forms white needles melting at 283°, and subliming without decomposition; it dissolves readily in alcohol, sparingly in water. It is identical with the acid obtained by oxidising α- and β-bromocymene with nitric acid. The *ammonium salt* forms fine, colourless, asymmetric crystals ($a : b : c$ = 1·5030 : 1 : 0·9753; β = 70°) which decompose at 100°. The *barium salt* is white; the *copper* and *silver salts* form respectively light-blue and white precipitates. The acid may also, although less conveniently, be obtained by saponifying *parabromometacyanobenzoic acid*, $CN{\cdot}C_6H_3Br{\cdot}COOH$, with concentrated hydrochloric acid. This acid is obtained from parabromometamidobenzoic acid by the action of sodium nitrite on an aqueous solution in the presence of copper cyanide. It forms white needles melting at 186°, and subliming without decomposition. It dissolves readily in hot water and alcohol; the copper and lead salts form respectively light-green and yellowish-brown precipitates. Asymmetrical bromisophthalic acid yields the corresponding hydroxy-acid with alkalis or alkaline carbonates, and with ammonia the corresponding amido-acid.

Parabromometasulphobenzaldehyde,

$$SO_3H{\cdot}C_6H_3Br{\cdot}CHO\ [Br : SO_3H : COH = 4 : 3 : 1],$$

is obtained as the *barium salt*, $(C_7H_4BrSO_4)_2Ba + 5H_2O$, by heating parabromobenzaldehyde with fuming sulphuric acid at 150°, and saturating with barium carbonate. It does not lose all its water until heated to 220°. When boiled with aqueous sodium carbonate, it yields the sodium salt of parahydroxymetasulphobenzaldehyde, $SO_3Na{\cdot}C_6H_3(ONa){\cdot}CHO$. C. F. B.

Friedel-Crafts' Synthesis. By M. Schöpff (*Ber.*, **24**, 3766—3770).—When haloïd derivatives of benzene are treated with acetic or benzoic chloride in the presence of aluminium chloride, the acetyl or benzoyl group takes the para-position relatively to the halogen, forming respectively parabromacetophenone, $C_6H_4Br{\cdot}COMe$ (the *hydrazone* of which, $C_6H_4Br{\cdot}CMe{:}N_2HPh$, forms yellowish plates melting at 126°), and parachlorobenzophenone, $C_6H_4Cl{\cdot}COPh$. If the para-position is already occupied, no reaction occurs, as in the case of paradibromo- and paradiiodo-benzene, and of 1 : 4-dibromonaphthalene.

With parabromobenzoic chloride and bromobenzene, the reaction takes place much less easily, and besides diparabromobenzophenone (the hydrazone of which, $C(C_6H_4Br)_2{:}N_2HPh$, forms yellow plates melting at 138°), some monobromobenzophenone is also formed.

The homologues of the halogen benzenes react, although less easily than these, if the para-position to the halogen is still unsubstituted; in the opposite case, no reaction takes place, as, for example, with parabromotoluene and unsymmetrical bromometaxylene, $C_6H_3BrMe_2$ [Br : Me_2 = 1 : 2 : 4]. Orthobromotoluene and acetic chloride yield *parabromometatoluyl methyl ketone*,

$$C_6H_3BrMe{\cdot}COMe \text{ [Br : Me : COMe = 4 : 3 : 1]},$$

as a yellowish oil with a feeble-greenish fluorescence boiling at 269—272°; when oxidised with permanganate, it yields parabromometatoluic acid. Bromoparaxylene and acetic chloride yield a small quantity of *bromoparaxylyl methyl ketone*, $C_6H_2BrMe_2{\cdot}COMe$ [Br : Me_2 : COMe = 4 : 3 : 6 : 1], which melts at 39°. C. F. B.

Deoxybenzoïns. By H. Wege (*Ber.*, **24**, 3540—3542).—*Benzyl orthoxylyl ketone*, $CH_2Ph{\cdot}CO{\cdot}C_6H_3Me_2$, prepared by Friedel and Crafts' method from orthoxylene and phenylacetic chloride, crystallises in yellow plates, melts at 95°, and boils at 210—220° under a pressure of 25 mm.; it is soluble in alcohol, ether, and light petroleum, and its *oxime* crystallises from light petroleum in lustrous, colourless needles. The *benzyl* derivative, $CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}C_6H_3Me_2$, obtained by boiling the ketone with an alcoholic solution of benzyl chloride and sodium ethoxide, crystallises from light petroleum in lustrous needles melting at 75°. The *isobutyl* derivative, $C_4H_9{\cdot}CHPh{\cdot}CO{\cdot}C_6H_3Me_2$, forms colourless or yellowish crystals, and melts at 91·5°.

Benzyl metaxylyl ketone is a thick, yellow oil, boils at 206—208° under a pressure of 22 mm., and is readily soluble in ether, but more sparingly in alcohol; its *benzyl* derivative boils at 365—375°.

Benzyl paraxylyl ketone boils at 220—230° under a pressure of 26 mm.; its *oxime*, $C_{16}H_{17}NO$, melts at 99°, its *hydrazone* at 96°, and its *benzyl* derivative at 60·5°. F. S. K.

Stereochemical Isomerism of Nitrogen Compounds. By A. Hantzsch and F. Kraft (*Ber.*, **24**, 3511—3528).—The authors have prepared a number of compounds, other than oximes, having the general formula $\frac{X}{Y}{>}C{:}NZ$, with the object of ascertaining whether such substances are capable of existing in stereochemically isomeric forms; if such were the case, there would be strong grounds for thinking that Auwers and Meyer's explanation of the isomerism of oximes is incorrect, because their hypothesis is based on the supposition that this isomerism is due to the peculiar constitution of hydroxylamine.

Paramethoxybenzhydrylamine, $NH_2{\cdot}CHPh{\cdot}C_6H_4{\cdot}OMe$, is obtained when either of the stereochemically isomeric paramethoxybenzophenoneoximes is reduced with sodium amalgam in the cold; it is a thick, optically-inactive oil, yields a sparingly soluble crystalline

hydrochloride melting at 191°, and a crystalline *acetyl* derivative which melts at 159°. The formation of a base isomeric with the above was not observed.

Imidobenzophenone hydrochloride, $CPh_2{:}NH,HCl$, is formed when benzophenone chloride (1 mol.) is heated with ethyl amidoformate (3 mols.) at about 130° until the evolution of hydrogen chloride ceases; it is a colourless, crystalline powder, sublimes when heated, and is insoluble in ether and benzene, and only moderately easily soluble in chloroform; it is quickly decomposed by cold water, yielding benzophenone and ammonium chloride. *Imidobenzophenone*, prepared by passing anhydrous ammonia into a chloroform solution of the hydrochloride, is a colourless oil, and is decomposed by water.

Paramethoxybenzophenone chloride, $CPhCl_2{\cdot}C_6H_4{\cdot}OMe$, can be obtained by warming paramethoxybenzophenone with slightly more than the theoretical quantity of phosphorus pentachloride. It crystallises in colourless plates, melts at 54°, and is readily soluble in benzene, chloroform, and ether; it is decomposed by warm water and by alcohol into hydrochloric acid and paramethoxybenzophenone.

Paramethoxybenzophenoneparachloraniline,

$$OMe{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}C_6H_4Cl,$$

is formed when the preceding compound (1 mol.) is warmed with parachloraniline (3 mols.) in chloroform solution. It crystallises in yellow plates, melts at 104°, and is readily soluble in benzene, ether, and chloroform, but more sparingly in alcohol; it is quickly decomposed into its components by hot dilute acids, but is not acted on by boiling water. All attempts to obtain an isomeride of this compound were unsuccessful.

Paramethoxybenzophenoneparatoluidine, $OMe{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}C_6H_4Me$, prepared in like manner, separates from chloroform in yellow crystals, melts at 96°, and resembles the preceding compound in its behaviour with acids. The chloroform mother liquors obtained in the preparation of this compound yield, on evaporation, not inconsiderable quantities of an oily product which does not crystallise when kept at 0°; it is possible that this oil contains an isomeride of the crystalline product (m. p. 96°).

Paramethoxybenzophenone-β-naphthylamine, $OMe{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}C_{10}H_7$, prepared from paramethoxybenzophenone chloride and β-naphthylamine, is a crystalline compound melting at 132°, but the products obtained in like manner from benzylamine and from paramidophenol are oils, as is also the condensation product of paratolyl phenyl ketone chloride with paratoluidine.

An additive product of the composition $OH{\cdot}CHPh{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$ is obtained, together with the condensation product immediately described below, when metamidobenzoic acid is shaken with water and benzaldehyde; it separates from ether in crystals, is readily soluble in chloroform, and is decomposed by warm dilute hydrochloric acid. The condensation product $CHPh{:}N{\cdot}C_6H_4{\cdot}COOH$ is gradually deposited from the mother liquors of the preceding compound; it is a yellowish, microcrystalline powder melting at 119°; the formation of an isomeride of this condensation product was not observed.

Benzophenoneparamidobenzoic acid, $CPh_2{:}N{\cdot}C_6H_4{\cdot}COOH$, prepared by heating benzophenone chloride with paramidobenzoic acid in chloroform solution, crystallises from chloroform in yellow prisms, melts at 240°, and is only sparingly soluble in ether, benzene, and cold alcohol, but moderately easily in hot alcohol, and very readily in chloroform; it is slowly decomposed by cold alcohol, and quickly by boiling dilute acids, yielding benzophenone and the amido-acid.

Paramethoxybenzophenoneparamidobenzoic acid, $C_{21}H_{17}NO_3$, is formed when paramethoxybenzophenone chloride is treated with paramidobenzoic acid in chloroform or toluene solution; it crystallises in yellow plates or microscopic needles, melts at 216°, and resembles the preceding compound in its behaviour with solvents and with dilute acids. The chloroform mother liquors from this compound contain a substance melting at about 164°; this, and the fact that the crude condensation product has no well-defined melting point, whilst that obtained from benzophenone chloride under like conditions melts quite sharply at 240°, lead the authors to conclude that possibly an isomeric paramethoxybenzophenoneparamidobenzoic acid is produced in the above reaction.

Two isomeric *hydrazones* of the composition $C_{20}H_{18}N_2O$, are produced when paramethoxybenzophenone chloride (1 mol.) is gradually added to a chloroform solution of phenylhydrazine (3 mols.); after keeping for some hours, the filtered solution is evaporated at the ordinary temperature, and the two products separated by fractional crystallisation. The one melts at 132°, crystallises from alcohol in small prisms, and is only sparingly soluble in cold alcohol, but moderately easily in ether, and very readily in chloroform and benzene; it is decomposed into its components by concentrated hydrochloric acid. The other hydrazone, which forms at the most only about 10 per cent. of the crude product, is a colourless powder, and melts at 90°; it resembles its isomeride very closely in appearance, and has approximately the same solubilities, except that it is much more readily soluble in ether. The only notable difference in chemical properties is, that the compound of lower melting point is less stable than the other, and resinifies more readily; under certain conditions, the compound of lower melting point seems to be converted into the isomeride. F. S. K.

Formation of Rosaniline. By B. Goldberg (*Ber.*, **24**, 3552—3553).—Bidet's statement (Abstr., 1889, 595) that a mixture of pure (thiophen-free) aniline, orthotoluidine, and paratoluidine only yields traces of rosaniline on heating with arsenic acid is incorrect; the author's experiments have shown that, practically, the same quantity of rosaniline is obtained from the thiophen-free, as from the commercial bases. F. S. K.

New Method of Formation of Desaurins. By V. Meyer and H. Wege (*Ber.*, **24**, 3535—3536).—Desaurin can be easily prepared by mixing deoxybenzoïn (1 mol.) with finely-divided potassium hydroxide (4 mols.), and boiling the mixture with carbon bisulphide (15—20 parts) for $2\frac{1}{2}$ hours; the carbon bisulphide is then distilled, the residue washed with alcohol and ether successively until the

washings are no longer coloured red, and then recrystallised from chloroform or xylene; the yield of the pure product is about 45 per cent. of the deoxybenzoïn employed. F. S. K.

Studies in the Induline Group. By O. Fischer and E. Hepp (*Annalen*, **266**, 249—263; compare Abstr., 1891, 1044).—When phenylinduline is heated at 160—170° for 5—6 hours with glacial acetic acid (5 parts) and 20 per cent. hydrochloric acid (20—30 parts), or dilute (1 : 5) sulphuric acid, it yields aniline, a base of the composition $C_{24}H_{19}N_3O$, benzeneindone, a hydroxy-compound of the composition $C_{18}H_{14}N_2O_2$, and a small quantity of a brownish-red substance; these products are isolated as follows:—The brownish-red solution is filtered from a considerable quantity of a brown, crystalline substance, which consists essentially of the hydrochloride of the base $C_{24}H_{19}N_3O$, but contains also a small quantity of the brownish-red substance; the last-named compound is probably a salt of carbazolefluorindine (*loc. cit.*), judging from the fluorescence of its solutions; it can be easily separated from the other hydrochloride, owing to its insolubility. The acid filtrate is then treated with excess of alkali, the precipitated benzeneindone separated by filtration, the alkaline solution treated with acetic acid, and the precipitated hydroxy-compound extracted by shaking with ether.

The *base* of the composition $C_{24}H_{19}N_3O$, obtained by decomposing the hydrochloride with alcoholic soda, crystallises from hot benzene in small, brown crystals having a steel-blue reflex; it melts at about 218° with evolution of a red vapour, and, when heated more strongly, it is converted into the brownish-red substance referred to above. It dissolves in glacial acetic acid and in dilute mineral acids yielding brownish-red, in concentrated hydrochloric acid and sulphuric acid yielding dirty-violet, solutions; when heated with concentrated hydrochloric acid, it is decomposed into aniline and the hydroxy-compound referred to above, and more fully described below.

The *hydroxy*-compound of the composition $C_{18}H_{14}N_2O_2$ is obtained in reddish-yellow crystals on evaporating its ethereal solution (see above); it crystallises from benzene or alcohol in brownish-yellow prisms or plates, gives off a brownish-red vapour when heated at 230°, and melts at about 280°; it imparts to textile materials a brownish-orange colour. It dissolves in concentrated sulphuric acid with a brownish-yellow coloration; its *hydrochloride* crystallises in thick prisms having a greenish-blue reflex, and is decomposed by water.

Benzeneindone, $C_{18}H_{12}N_2O$, crystallises from alcohol in lustrous, well-defined plates, dissolves in benzene and alcohol with a yellow, in dilute hydrochloric acid with a rose-red, and in concentrated sulphuric acid with a green, coloration; when distilled with zinc-dust, it yields phenazine (m. p. 171°) and benzene.

A compound of the composition $C_{18}H_{15}N_3O_2$ is formed, together with a violet base, aniline, and a sparingly soluble, almost black compound, when amidophenylinduline sulphate is heated with dilute sulphuric acid for 4—5 hours at 160—170°; the acid solution is filtered from the sparingly soluble sulphate of the violet base, mixed with soda, again filtered, the filtrate acidified with acetic acid,

and the precipitate recrystallised from 70 per cent. alcohol, from which it separates in small, nodular crystals, or in plates, showing a green reflex. It sinters together at about 230°, and melts completely at 270—280° with evolution of brown vapours; it dissolves in benzene, yielding an orange-red solution which shows a green fluorescence, and its solution in acetic acid is rose-red, that in concentrated sulphuric acid greenish-brown. The *sulphate* crystallises from hot, dilute sulphuric acid in red needles, and is moderately easily soluble in water.

Phenylamidophenylinduline, $C_{30}H_{22}N_4$, is formed, together with much smaller quantities of anilidophenylamidophenylinduline (see below), when amidophenylinduline is heated with aniline (2 parts) at 150—160° for some hours. It crystallises from hot benzene in small nodules or plates having a green reflex, and melts at 245—250°; its solution in benzene is reddish-violet, that in alcohol, blue, and that in concentrated sulphuric acid, greenish-blue. The *hydrochloride*, $C_{30}H_{22}N_4,HCl$, forms lustrous, greenish crystals. This induline can also be obtained by heating an alcoholic solution of phenylamidoazobenzene (136 grams) with aniline (140 grams) and aniline hydrochloride (65 grams) at 150—160° for a day; the yield of the hydrochloride is about 100 grams.

Anilidophenylamidophenylinduline, $C_{36}H_{27}N_5$, is best prepared by heating a mixture of azobenzene (12 parts), aniline (48 parts), aniline hydrochloride (24 parts), and nitrobenzene (12 parts) for eight hours at 170°. It crystallises from boiling xylene in nodules or plates having a green reflex, and melting at 286—288°; it is more sparingly soluble than any other known induline. The *hydrochloride* crystallises in lustrous needles, and dissolves in alcohol with a greenish-blue coloration.

The molecular weight of phenylinduline was determined by Raoult's method in benzene solution; the results were in accordance with those required by a compound of the molecular formula $C_{24}H_{17}N_3$.

F. S. K.

Homologues of Acridine. By A. Volpi (*Gazzetta*, **21**, ii, 228—237).—*Ethylacridine*, $C_6H_4<\overset{CEt}{\underset{N}{|}}>C_6H_4$, is prepared by Bernthsen's method (Abstr., 1884, 1356) by the action of propionic acid on a mixture of diphenylamine and zinc chloride. When pure, it crystallises in lustrous, white plates with a yellowish tinge, melts at 116°, and dissolves freely in alcohol, benzene, and light petroleum, forming solutions with a blue fluorescence; it is only very sparingly soluble in water. The dilute solutions of its salts all have a green fluorescence. The *platinochloride*, $(C_{15}H_{13}N)_2,H_2PtCl_6$, forms minute, yellow crystals, which decompose at 215° without melting. The *aurochloride*, $C_{15}H_{13}N,HAuCl_4$, crystallises in needles melting at 170°. The *hydrochloride*, $C_{15}H_{13}N,HCl$, crystallises in yellow, monoclinic prisms, $a : b = 1{\cdot}5199 : 1$; $\beta = 83° 07'$. It dissolves freely in water, and the solution is brownish-yellow when concentrated, and yellow, with a green fluorescence, when dilute. It is readily soluble in alcohol, and decomposes when heated, without previous melting;

the *sulphate*, $(C_{15}H_{13}N)_2,H_2SO_4$, is pale-yellow in colour, and melts at 210°.

Propylacridine, $C_6H_4<\overset{CPr}{\underset{N}{|}}>C_6H_4$, prepared in a manner similar to the previous compound, by the action of butyric acid on a mixture of diphenylamine and zinc chloride, crystallises from alcohol in colourless, monoclinic plates, $a : b : c = 2{\cdot}015 : 1 : 1{\cdot}998$; $\beta = 61° 07'$. It melts at 72—75°, dissolves freely in alcohol, and is almost insoluble in water; its solutions have the characteristic green fluorescence, and in other respects it has the general properties of the acridines. The *hydrochloride*, $C_{16}H_{15}N,HCl$, forms yellow crystals which, when heated, decompose without previously melting; the *sulphate*, $C_{16}H_{15}N,H_2SO_4$, forms greenish-yellow crystals, readily soluble in water and alcohol, but insoluble in ether. It darkens at 245°, and melts at 249°.

Pentadecylacridine, $C_6H_4<\overset{C(C_{15}H_{31})}{\underset{N}{|}}>C_6H_4$, is prepared from palmitic acid by the same method as the preceding compounds. It separates from alcohol as a crystalline mass of a buttery consistency, but may be obtained in white or yellowish plates by slowly evaporating the alcoholic solution. It melts at 65°, and dissolves in alcohol, ether, benzene, and light petroleum, but not in water. The alcoholic solution of the base has a blue fluorescence, whilst the alcoholic solutions of its salts have a green fluorescence, and are decomposed by water. The *platinochloride*, $(C_{28}H_{39}N)_2,H_2PtCl_6$, forms minute, orange-yellow crystals melting at 185°. The *hydrochloride*, $C_{28}H_{39}N,HCl$, is a yellow substance which melts at 79°, dissolves in alcohol, and is decomposed by water. The *sulphate*, $C_{28}H_{39}N,H_2SO_4$, crystallises in tufts of yellowish-red needles, melts at 150—151°, and dissolves in alcohol and benzene, but is insoluble in ether, and is decomposed by water; its solutions have a feebly acid reaction.

Stearic acid also yields an acridine by Bernthsen's reaction, so that if the reaction does not apply to the entire series of fatty acids, the limit must lie beyond stearic acid. Acridines may also be prepared from lactic, succinic, and tartaric acids, and will be described by the author in a future paper. S. B. A. A.

Methylcarbazacridine. By D. Bizzarri (*Gazzetta*, **21**, ii, 158—163).—*Methylcarbazacridine*, $\overset{N—C_6H_3}{\underset{MeC—C_6H_3}{|\times|}}$, is obtained by a method analogous to that used for the preparation of phenylcarbazacridine (Abstr., 1891, 219). A mixture of carbazole (8 grams), glacial acetic acid (7 grams), and zinc chloride (15 grams) is heated at 150—155° in a sealed tube for eight hours. The bluish-green, pitchy product is extracted with boiling absolute alcohol, the liquid filtered into concentrated ammonia solution, and diluted with water. The bright-red precipitate is collected, washed, dried, and repeatedly extracted with dilute alcohol (47 per cent.); on cooling, the solution deposits a yellowish-white substance, which, after being washed with dilute alcohol, dried, and dissolved in the least possible quantity of

glacial acetic acid, is reprecipitated by ammonia, and finally fractionally crystallised from benzene and alcohol. Minute, colourless, uniaxial rhombohedra are thus obtained, soluble in acetic acid, sparingly so in alcohol, benzene, ether, chloroform, and carbon bisulphide, and insoluble in water and light petroleum. When heated, the substance shrinks at 150°, softens at 175°, melts at 178°, and decomposes at higher temperatures. When its acetic acid solution is treated with zinc-dust, filtered, and the filtrate precipitated with water, a white, crystalline powder is obtained, melting with decomposition at 206°; this dissolves in acetic acid, yielding a colourless solution, which, on treatment with potassium dichromate, gives the characteristic cherry-red colour of the original substance. Acids also, especially hydrochloric and sulphuric, rapidly reconvert it into methylcarbazacridine, of which it is, doubtless, the hydro-derivative. The compounds of methylcarbazacridine with acids have the same instability as the corresponding phenylcarbazacridine compounds, being decomposed by water, alcohol, excess of acids, or by drying. The *hydrochloride* forms beautiful, indigo-blue plates, the *sulphate* greenish-blue plates, the *nitrate* light-blue plates, and the *chromate* brownish-green plates. Picric acid forms an unstable compound crystallising in ruby-red needles. Methylcarbazacridine is obtained in small quantity by heating acetylcarbazole with zinc chloride for two hours at 150—155°, and proceeding as above indicated. The aqueous alcohol used in the preparation of the substance retains in solution a compound melting at 137—138°, and crystallising in minute prisms, soluble in acetic acid. W. J. P.

Aromatic Nitriles. By F. J. Zinsser (*Ber.*, **24**, 3556—3557; compare Freund and Immerwahr, Abstr., 1890, 1407).—A more convenient method for preparing diphenylacetic acid than that usually adopted is to boil benzilic acid with hydriodic acid (b. p. 127°) and a little amorphous phosphorus for four hours; the nitrile of this acid is best prepared by quickly distilling a mixture of the amide and phosphorus sulphide from a small retort.

Diphenylacetonitrile does not react with fatty halogen compounds under various conditions; on reduction with sodium and amyl alcohol, it is converted into diphenylmethane and hydrogen cyanide. When phenylcinnamonitrile, CHPh:CPh·CN, is treated with sodium and amyl alcohol, it yields a large quantity of dibenzyl.

F. S. K.

1 : 3′ : 4-Dichloronaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **24**, 3477—3479).—1 : 3′ : 4-*Dichloronaphthalenesulphonic acid* is obtained by dissolving 1 : 3′-dichloronaphthalene (m. p. 48°) in a mixture of fuming and concentrated sulphuric acid (equal parts) and gently warming, when a pasty mass is produced, which, on dissolution in water, yields microscopic needles of the acid; it is very sparingly soluble in dilute sulphuric acid. A second product, probably a disulphonic acid, is also obtained in small quantity. The *potassium* salt crystallises in flat needles and tablets of a silvery lustre with 1 mol. H_2O; the *ammonium* salt resembles it; the *sodium* salt forms thin needles with 3 mols. H_2O; the *silver* salt lustrous scales with

1 mol. H_2O; the *calcium* and *barium* salts crystallise with 3 mols. H_2O; whilst the *zinc* salt crystallises with 5 mols. H_2O. All these salts are readily soluble in boiling water, and, for the most part, sparingly so in cold water. The *lead* salt crystallises with 4 mols. H_2O; the *copper* salt with 6 mols. H_2O; whilst the *methyl* and *ethyl* salts form delicate needles and melt at 138° and 154° respectively. The *sulphonic chloride* crystallises from glacial acetic acid in needles, and melts at 151°, whilst the *sulphonamide* forms long, flat, satiny needles, and melts at 217°. 1 : 4 : 3′-Trichloronaphthalene (m. p. 65°) is formed when the sulphonic chloride is heated with an excess of phosphorus pentachloride. A. R. L.

1 : 2-Amidonaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **24**, 3472—3477).—Landshoff and Meyer (D.-R.P. 56,563) describe a naphthylaminesulphonic acid, obtained by heating at 200—250° an alkali salt of naphthionic acid which contains the amido-group in an α-position. The sulpho-group must occupy the β-position adjacent to the amido-group, as it can be converted into 1 : 2-dichloronaphthalene (m. p. 34°). The new acid forms long, anhydrous needles or small, rhombic crystals, $a : b : c = 0{\cdot}79401 : 1 : 0{\cdot}36429$, and is more soluble than its isomeride, dissolving in 34 parts of boiling water and 225 parts of cold; if allowed to slowly crystallise at the ordinary temperature, long needles containing $\frac{1}{2}$ mol. H_2O are obtained. The *potassium* salt, sparingly soluble in cold water, the *sodium* salt, dissolving in 60 parts of cold water, the *ammonium* salt, readily soluble in water, the *silver* salt, a white, sparingly soluble precipitate, and the *calcium* salt, sparingly in water, are anhydrous, whilst the *magnesium* salt crystallises with 8 mols. H_2O, the zinc salt with 5 mols. H_2O, and the *barium*, *lead*, and *manganese* salts with 1 mol. H_2O. The *acetyl* derivative dissolves easily in water and separates in small, lustrous needles containing 1 mol. H_2O. The *diazosulphonic acid* is a greenish, crystalline powder, and yields a *hydrazinesulphonic acid* crystallising in micacous plates. The chlorosulphonic acid, obtained by boiling the diazo-derivative with cuprous chloride, crystallises in plates of a silvery lustre, and yields a *sulphonic chloride* melting at 80°, anhydrous *potassium*, *sodium*, *silver*, and *barium* salts, a *calcium* salt containing 1 mol. H_2O, and an *ethyl* salt crystallising in small, colourless needles, and melting at 104°. 1 : 2-Dichloronaphthalene passes over on distilling the chlorosulphonic acid with an excess of phosphorus pentachloride. 1 : 2-*Naphtholsulphonic acid* is produced by adding the diazo-derivative to boiling dilute sulphuric acid, and is purified by first converting it into the barium salt and then into the lead salt; it forms small, lustrous, rhombic tablets, is readily soluble in boiling water, sparingly in cold, and does not melt at 250°; its solution gives with ferric chloride an indigo-blue colour, which soon changes to dirty red. The *sodium* salt is readily soluble in water; the *lead* and *calcium* salts crystallise with 1 mol. H_2O, and are sparingly soluble in water, whilst the *barium* salt crystallises with $1\frac{1}{2}$ mols. H_2O, and is also sparingly soluble in water. Further experiments are in progress. A. R. L.

Nitrosonaphtholsulphonic Acids. By O. Hoffmann (*Ber.*, **24**, 3741—3746).—*Sodium ferrinitrosonaphtholsulphonate*,

$$Fe(NO\cdot C_{10}H_5O\cdot SO_3Na)_3\ [O : NO : SO_3 = 1 : 2 : 4],$$

is prepared by adding ferric chloride in excess to nitroso-α-naphtholsulphonic acid and treating the solution with soda; the compound crystallises from water in dark-green plates. The corresponding *potassium salt*, $Fe(NO\cdot C_{10}H_5O\cdot SO_3K)_3$, is more unstable than the sodium compound, and does not give constant analytical results.

Cupric nitrosonaphtholsulphonate, $C_{10}H_5O\lessdot^{NO}_{SO_3}\!>Cu + 3H_2O$, is obtained from nitroso-α-naphtholsulphonic acid and cupric sulphate, and crystallises in groups of brown needles. Nitroso-β-naphtholsulphonic acid gives an insoluble, amorphous precipitate with cupric sulphate.

Cupric ammonionitrosonaphtholsulphonate,

$$C_{10}H_5O\lessdot^{NO\cdot NH_3}_{SO_3\cdot NH_3}\!>Cu + H_2O,$$

is formed from nitroso-α-naphtholsulphonic acid and cupric ammoniosulphate, or by heating the preceding copper salt with ammonia, and crystallises in small, brown plates, which exhibit an intense, bronze lustre in reflected light. The compound from nitroso-β-naphtholsulphonic acid resembles the α-derivative in properties and composition.

Zinc ammonionitrosonaphtholsulphonate, $C_{10}H_5O\lessdot^{NO\cdot NH_3}_{SO_3\cdot NH_3}\!>Zn + + H_2O$ [O : NO : SO_3 = 1 : 2 : 4], crystallises in lustrous, brownish-red needles, which are somewhat soluble in dilute ammonia. The corresponding compound [O : NO : SO_3 = 2 : 1 : 3′] is deposited in yellowish-green, lustrous plates.

The *cadmium ammonio-salts* are crystalline; the α-naphtholsulphonic acid derivative is deposited in long, orange-coloured needles, whilst that from β-naphtholsulphonic acid is obtained in yellowish-green, microscopic plates.

All the above ammonio-derivatives decompose, with evolution of ammonia, on heating in aqueous solution.

Sodium nitrosonaphtholsulphonate, $NONa{:}C_{10}H_5O\cdot SO_3Na + 2H_2O$ [O : NO : SO_3 = 2 : 1 : 3′], is prepared by adding concentrated soda to a hot saturated solution of sodium nitroso-β-naphtholsulphonate, and crystallises in small, slender, green needles. J. B. T.

Hydroxyanthranol. By C. E. Linebarger (*Bull. Soc. Chim.* [3], **6**, 92—94).—Benzylhydroxyanthranol,

$$OH\cdot CH\lessdot^{C_6H_4}_{C_6H_4}\!>C(OH)\cdot CH_2Ph,$$

is best prepared by boiling for three hours a mixture of 5 parts of soda, 50 parts of water, 10 parts of zinc-dust, and 3 parts of anthraquinone, and then adding 2 parts of benzyl chloride in small portions and continuing the boiling for five hours. The product, after being purified by crystallisation from alcohol, is recrystallised from benzene. It then forms very pure but small prisms, melts at 60—61°, and

begins to decompose at 100°. It is insoluble in water, soluble in alcohol, benzene, and chloroform. Its solutions have a bluish fluorescence. Anthraquinone is obtained by oxidation with chromic acid in acetic solution. Benzylanthracene is obtained by reduction with hydriodic acid and amorphous phosphorus. The production of diacetylbenzylhydroxyanthranol, by boiling 3 parts of benzylhydroxyanthranol with 6 parts of sodium acetate and 20 parts of acetic anhydride for half an hour, proves the presence of two hydroxyl groups. The purified product forms small, greenish tables, insoluble in water, soluble in alcohol, very soluble in benzene. It melts at 126°. W. T.

Paranthracene. By K. Elbs (*J. pr. Chem.* [2], **44**, 467—469).—The paranthracene was prepared by exposing a benzene solution of 90 per cent. anthracene, saturated at 40—60°, for a week to sunshine, and then gently warming it on the water-bath to dissolve any anthracene which might have crystallised out together with the paranthracene. The precipitate was then filtered, washed with benzene, and crystallised either from boiling xylene or dimethylaniline. From xylene, paranthracene generally crystallises in colourless, lustrous needles, and from dimethylaniline in laminæ. The crystals melt, but not sharply, between 272° and 274°, and become converted into anthracene. Paranthracene does not fluoresce, whether as solid or in solution; it remains unchanged at 260°, and when a solution of it in dimethylaniline is heated; on the other hand, a solution of it in naphthalene and in diphenylamine rapidly becomes fluorescent from its conversion into anthracene, the former solution when boiled, and the latter when heated at 260°.

The solubility of paranthracene in various solvents at their freezing point is very slight; naphthalene proved the best solvent for determining the molecular weight of paranthracene by the cryoscopic method, and even this only dissolves 0·229 per cent. at its melting point. A large number of determinations were made with the solution in naphthalene, and the results showed values varying between 276 and 344 as the molecular weight of paranthracene, whose formula may, therefore, be allowed to be $(C_{14}H_{10})_2$. Graebe and Liebermann assert that paranthracene is stable towards bromine in sunlight. The author finds that a mixture of paranthracene (1 part), bromine (10 parts), and carbon bisulphide (100 parts), exposed to sunlight, rapidly evolves hydrogen bromide, and yields dibromanthracene tetrabromide. Anthracene behaves similarly under the same circumstances, although statements as to the bromination of anthracene take no account of the fact. A. G. B.

Terpenes and their Derivatives. By J. W. Brühl (*Ber.*, **24**, 3701—3737; compare this vol., p. 200).—This paper describes some of the physical constants of the compounds described in the previous communication.

The specific gravity was determined at 20° and compared with water at 4°. The refractive index (n) was usually determined for the potassium, sodium, lithium, and thallium flames, and also for the

lines in the hydrogen spectrum, Hα, Hβ, Hγ, Hδ. The term "specific dispersion" is applied to the difference in the specific refractive powers of the compounds in the region of the spectrum between Hγ and Hα. $\mathfrak{M}\alpha$ denotes the molecular refractive power for the hydrogen line α.

The sp. gr. of menthyl ethyl ether, $C_{10}H_{19}OEt$ = 0·8513; $\mathfrak{M}\alpha$ = 56·96, and the molecular dispersion = 1·38; these numbers agree closely with the theoretical values. Ethyl camphor could not be obtained quite pure; its sp. gr. = 0·9372; $\mathfrak{M}\alpha$ = 53·40; $\mathfrak{M}n_a$ = 53·64; molecular dispersion = 1·29; the compound, therefore, contains no ethylene linkage.

Ethyl camphocarboxylate, like the preceding compound, contains no ethylene linkage; the sp. gr. = 1·0563; $\mathfrak{M}\alpha$ = 59·48; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 1·45. The molecular dispersion of these compounds is thus seen to be unaffected by the closing of an open chain; in this respect it resembles molecular refraction, nor is it influenced by a para-linkage in the benzene nucleus; that is to say, by the formation of a double tetramethylene ring. Ethyl camphocarboxylate ethyl ether is represented by the formula already given, and is not a camphordicarboxylic acid; its sp. gr. = 1·0759; $\mathfrak{M}\alpha$ = 76·92; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 2·20. The theoretical values are 74·61 and 1·177, the difference is probably due to experimental error.

Bornyl ethyl ether, $C_{10}H_{17}$·OEt, was prepared by the mutual action of borneol, sodium, and ethyl iodide, and also from camphor by Baubigny's method; the sp. gr. = 0·9008; $\mathfrak{M}\alpha$ = 54·88; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 1·31.

Bornyl methyl ether, $C_{10}H_{17}$·OMe, like the preceding compound, has no ethylene linkage, the sp. gr. = 0·9162; $\mathfrak{M}\alpha$ = 50·36; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 1·26.

Bornyl methylene ether, $(C_{10}H_{17}O)_2CH_2$, crystallises in rhombic prisms, $a : b : c$ = 0·9134 : 1 : 0·565; the sp. gr. = 1·0735; $\mathfrak{M}_{H\alpha}$ = 92·77; $\mathfrak{M}_{H\gamma} - \mathfrak{M}_{H\alpha}$ = 2·16; this value was obtained indirectly; the number required by theory is 2·14, and it appears to be the first known example of a compound crystallising in any but the regular system, the molecular refraction and molecular dispersions of which agree with the values deduced from its chemical composition and constitution; for details of the measurements and calculations, the original paper should be consulted.

The constants for diethyl camphorate also agree with theoretical numbers; the sp. gr. = 1·0298; $\mathfrak{M}\alpha$ = 67·32; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 1·57. The compound contains no ethylene linkage.

On account of the extreme viscosity of ethyl hydrogen camphorate, the sp. gr. was determined by means of the vacuum pyknometer (Abstr., 1891, 520); the sp. gr. = 1·09977; $\mathfrak{M}\alpha$ = 57·84; $\mathfrak{M}\gamma - \mathfrak{M}\alpha$ = 1·37; the acid, therefore, contains no ethylene linkage, and the physical properties agree with the formula already proposed for it. The molecular heat of combustion of camphoric acid = 1243·6 cal. and of camphoric anhydride = 1252·4 cal.; the small difference between these numbers indicates that the carboxyl groups are in the ortho-position.

The author considers that the low electrical conductivity of camphoric acid is the only fact which can be urged against his formula;

after pointing out that this may be due to the presence of the basic group $CH_2 \cdot CH_2$, he discusses the general effect of substitution on the electrical conductivity of acids, and enumerates a number of apparent anomalies; since no analogue of camphoric acid is known in the succinic acid series, it is impossible to foresee how the electrical conductivity would be affected by the introduction of the group C_2H_4. J. B. T.

Crystalline Products from Lemon and Bergamot Oils. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 30—33; compare Tilden and Beck, Trans., 1890, 323).—The residue from the distillation of lemon oil at a pressure of 10 mm. is dissolved in light petroleum, and this solution deposits nodular crystals of the composition $C_{10}H_{10}O_4$, which are purified by recrystallisation from anhydrous ether, and then form a white, inodorous powder which melts at 144°, and neither decomposes nor sublimes when heated to 240°. Sulphuric acid colours this substance, which is, perhaps, hesporetic acid, golden-yellow; a trace of nitric acid converts this to green, or a trace of potassium permanganate to blue, which subsequently becomes green. On evaporation, the light petroleum leaves a butter-like mass, melting about 50°, and this, after purification by recrystallisation from alcohol, has a lemon-like odour, and gives a dark brown coloration (this vol., p. 386) with ammoniacal manganous solutions, differing in this respect from the substance $C_{10}H_{10}O_4$. Bergamot oil, when similarly treated, affords white, crystalline needles which melt at 184°, sublime at 230—240°, and have the centesimal composition C 65·24, H 3·78, O 30·98. This substance does not appear to be the bergaptene of Mulder and Ohme, which melts at 206°. T. G. N.

Action of Hydriodic Acid and Amorphous Phosphorus on Picrotin. By A. Oglialoro and O. Forte (*Gazzetta*, **21**, ii, 213—215).—*Picrotoxic acid*, $C_{15}H_{18}O_4$, is obtained by warming a mixture of picrotin (prepared by the action of potash on picrotoxin), amorphous phosphorus, and hydriodic acid, allowing the brisk effervescence which takes place at first to subside, and then boiling for about 10 hours in a reflux apparatus. On diluting the product with water, steam-distilling, and filtering the residue, the filtrate, on cooling, leaves a white deposit of picrotoxic acid. This crystallises from dilute alcohol in lustrous, white needles, melts at 134°, dissolves readily in alcohol, but only sparingly in hot water. It has a feebly acid reaction, and dissolves in alkalis, but is reprecipitated from its solutions on the addition of an acid. The *silver* salt, $C_{15}H_{17}O_4Ag$, is a white, crystalline powder, sensitive to light. The formation of this acid affords additional proof of the formula $C_{15}H_{18}O_7$ for picrotin. S. B. A. A.

Constituents of the Buds of Chrysanthemum Cinerariæfolium. By H. Thoms (*Chem. Centr.*, 1891, ii, 670—671; *Pharm. Centralhalle*, **32**, 471—472).—Continuing his examination of the constituents of the buds of *Chrysanthemum cinerariæfolium* (see also Abstr., 1891, 333), the author describes one of the new compounds, *pyrethrosin*,

more fully. The light petroleum extract of the buds was concentrated, and a golden-yellow, soft residue obtained, which, after being washed with alcohol, remained as colourless, bitter crystals. The crystals are elongated, rhombic octahedrons, melting at 188—189°. It is readily soluble in chloroform and in hot alcohol, less soluble in ether and light petroleum, insoluble in water. Its formula is $C_{34}H_{44}O_{10}$ (?). It dissolves in concentrated sulphuric acid with yellow or weak redish-brown coloration. In 25 per cent. hydrochloric acid, the substance becomes red or violet, and the solution is violet coloured; water precipitates yellow plates. The filtrate, after treatment with hydrochloric acid, does not reduce Fehling's solution, so that pyrethrosin cannot be considered as a glucoside; but if the yellow compound be treated with concentrated hydrochloric acid, and the solution be neutralised, it then reduces Fehling's solution. The author suggests that the yellow substance is nearly related to phloroglucinol, and that pyrethrosin is a phloroglucide. J. W. L.

Agrostemma Githago (Corn Cockle). By N. Kruskal and R. Kobert (*Chem. Centr.*, 1891, ii, 545—546; *Arb. pharm. Inst. Dorpat*, **6**, 89—145, 146—148).—The sapotoxin of *Agrostemma* has the same composition as those of *radix saponariæ albæ* and of quillaja bark, but differs from them in its physiological properties. Hydrolysis with acids causes the formation of glucose (4 mols.) and sapotoxin (1 mol.). The corn cockle contains about 6·17 per cent. on the average.

Agrostemma-sapotoxin has an irritating action on the mucous membrane of the nose, mouth, and eyes; it affects the nerves similarly to that of the quillaja bark. When in solution (1 : 15000), it dissolves blood corpuscles of both carnivorous and herbivorous animals. It appears to act differently on animals when taken inwardly, the Herbivoræ being relatively unaffected, provided that the doses are not too large and not taken for too great a length of time, whilst, on the other hand, the Carnivoræ are seriously affected and readily succumb to its action. On man it has an intermediate effect, but doses of 0·1 gram are sufficient to cause illness. The author points out that the bread which the Russian military authorities provide for the soldiers may contain as much as 0·5 per cent. of corn cockle, and this corresponds with a dose of about 6 grams of corn cockle per day, a quantity which may readily produce serious toxical effects.

Kobert points out that the simple term "saponin" is not sufficient, and the source from which it has been obtained should be stated, since the several different saponins have such varying physiological actions. The several saponins appear to belong to series of compounds which have different generic formulæ. Stütz's saponin, $C_{19}H_{25}(OH)_5O_5$, belongs to a series the formula of which would be $C_nH_{2n-8}O_{10}$. The lowest member of the series is isomeric with syringin, and has the formula $C_{17}H_{28}O_{10}$. J. W. L.

Constitution of the Ethylpyrrolines. By C. U. Zanetti (*Gazzetta*, **21**, ii, 163—173).—The author applies the method given by him (Abstr., 1891, 1387) for the determination of the constitution

of pyrroline derivatives to the case of the ethylpyrrolines obtained by the various known methods.

Ethylpyrroline (1 vol.), obtained by passing a mixture of equal volumes of ethyl alcohol and pyrroline through a heated tube containing zinc-dust (Abstr., 1890, 1428), is dissolved in alcohol (10 vols.) and boiled with the calculated quantities of hydroxylamine hydrochloride and anhydrous sodium carbonate for six hours. The solvent is distilled off under reduced pressure, the residue treated with cold, dilute aqueous potash, and the unaltered pyrroline extracted with ether. The solution is now saturated with carbonic anhydride, and again extracted with ether; on evaporating the ethereal solution, a syrup is left which solidifies almost completely after a time. The resinous matter is removed from this by washing with cold ether, and the residue dissolved in boiling ether; on cooling, the solution deposits a small quantity (0·2 gram from 11 grams of ethylpyrroline) of a *dioxime*, $C_6H_{12}N_2O_2$, which, after recrystallisation from ether, forms colourless scales, and melts at 134—135°. The ethereal solution, on concentration, yields a quantity (4 grams from 11 grams of ethylpyrroline) of an isomeric *dioxime*, which, on being repeatedly recrystallised from anhydrous ether, is obtained in splendid, colourless scales melting at 84—85°; this compound is very soluble in water, alcohol, benzene, and ethyl acetate, somewhat less so in ether. The formation of these two dioximes shows that the ethylpyrroline is a mixture of two isomerides.

The oxime melting at 84—85° (2 grams), when boiled with 30 per cent. aqueous potash (30 c.c.), gives off ammonia; the brownish-red solution thus obtained is saturated with carbonic anhydride, repeatedly extracted with ether to remove the unchanged oxime, and decolorised by animal charcoal. The solution is now exactly neutralised with sulphuric acid and evaporated to dryness, first on a water-bath and then in a vacuum. On extracting the residue with anhydrous ether free from alcohol, and evaporating the ethereal solution, a syrupy acid is left; this does not solidify, dissolves with effervescence in solutions of the alkaline carbonates, gives a violet coloration with ferric chloride, and yields an uncrystallisable hydrazone. With lead acetate solution, the ammonium salt gives a white precipitate, soluble in excess; with mercurous chloride, a white precipitate, rapidly changing to metallic mercury; with mercuric chloride, an opalescence; and with silver nitrate, in concentrated solution, a yellow precipitate rapidly changing to metallic silver. The acid is probably *normal propionylpropionic acid*, $CH_2Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, its *silver* salt having the composition $AgC_6H_9O_3$. The dioxime melting at 84—85° has, therefore, the constitution $CH_2Me{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}NOH$, and the pyrroline from which it is obtained must be α-ethylpyrroline. The dioxime melting at 134—135° is probably $NOH{:}CH{\cdot}CH_2{\cdot}CHEt{\cdot}CH{:}NOH$, and is derived from β-ethylpyrroline.

The ethylpyrroline obtained by the action of ethyl iodide on the potassium compound of pyrroline boils at the same temperature (163—165°) as the above, but, on treatment with hydroxylamine hydrochloride, yields nothing but a small quantity of the dioxime melting at 134—135°. The pyrroline obtained in this manner is,

therefore, β-ethylpyrroline, that obtained from alcohol and pyrroline being a mixture of α- and β-ethylpyrroline, boiling at the same temperature.

The above experiments fully agree with the authors' previous observation, that β-pyrroline derivatives are much more stable than α-pyrrolines. Diethylpyrroline yields no trace of oximido-compound on treatment with hydroxylamine hydrochloride. W. J. P.

Derivatives of Carbonyl Chloroplatinite. By F. Foerster (*Ber.*, **24**, 3751—3765; compare Abstr., 1891, 1162).—*Pyridine carbonyl chloroplatinite*, $COPtCl_2,C_5NH_5$, is obtained as a yellow oil by mixing an aqueous solution of pyridine with a hydrochloric acid solution of carbonyl chloroplatinite, $COPtCl_2$. It decomposes at 100°, forms a *hydrochloride*, $COPtCl_2,C_5NH_5,HCl$, and when treated with hydrobromic acid yields, not the hydrobromide, but the compound $COPtBr_2,C_5NH_5,HBr$. It also forms a very unstable *picrate*.

Dipyridine carbonyl chloroplatinosite, $\begin{matrix}COPtCl,C_5NH_5\\ \vdots\\ COPtCl,C_5NH_5\end{matrix}$, is obtained by mixing a fairly concentrated hydrochloric acid solution of carbonyl chloroplatinite with an alcoholic solution of pyridine, shaking to redissolve the precipitate first formed, and recrystallising from alcohol the crystals that finally separate. It forms, when pure, yellowish-green needles, dissolves readily in methyl and ethyl alcohol, chloroform, and benzene, very sparingly in ether, carbon bisulphide, and light petroleum, decomposes at 60°, and is decomposed by mere traces of moisture. In the reaction mentioned above, carbonic anhydride is evolved, and out of the mother liquor from the substance last described there can be obtained, by evaporation at the ordinary temperature, first lustrous, yellowish-green crystals of a double compound,

$$C_2O_2Pt_2Cl_2(C_5NH_5)_2,2PtCl_2(C_5NH_5)_2,$$

which dissolves without decomposition in hot hydrochloric acid, and can be dried at 100°. Then separate large, colourless, oblique prisms of *platodipyridine chloride*, $PtCl_2(C_5NH_5)_4 + 3H_2O$, and small, yellowish-brown needles, consisting for the most part of *platosopyridine chloride*, $Pt(C_5NH_5Cl)_2$, but containing also a little *platosemidipyridine chloride*, $PtCl(C_5NH_5)_2Cl$. Platosopyridine chloride forms, with dipyridine carbonyl chloroplatinosite, the double compound mentioned above, and from it, with excess of pyridine, the platodipyridine chloride was doubtless derived. Dipyridine carbonyl chloroplatinosite, when treated with chlorine, yields pyridine platinochloride, $(C_5NH_5)_2,H_2PtCl_6$, and hydroplatinochloric acid, H_2PtCl_6; when it is boiled with hydrochloric acid, platinum separates, and the hydrochlorides of pyridine carbonyl chloroplatinite and of pyridine are formed. A compound $COPtCl_2,(C_5NH_5,HCl)_2$ appears to be incapable of existence.

Analogous bromine compounds were obtained in a similar manner. *Pyridine carbonyl bromoplatinite*, $COPtBr_2,C_5NH_5$, forms yellow needles or plates melting at 78—79°; it dissolves readily in benzene, carbon bisulphide, ethyl acetate, and hot alcohol, more sparingly in cold alcohol, ether, and light petroleum; it is decomposed by hot

water. It forms a *hydrochloride*, $COPtBr_2,C_5NH_5,HCl$, and a very unstable *picrate*.

Dipyridine carbonyl bromoplatinosite, $(COPtBr)_2(C_5NH_5)_2$, is insoluble in most solvents, chloroform excepted. It forms triclinic crystals, which are decomposed by water or when heated to 60°. With hydrobromic acid, it behaves like the analogous chlorine compound with hydrochloric acid. *Platodipyridine bromide*,

$$PtBr_2(C_5NH_5)_4 + 3H_2O,$$

forms lustrous, rhombohedral crystals, which are soluble in water and alcohol, but not in ether; it decomposes at 130°, forming *platosopyridine dibromide*, $Pt(C_5NH_5Br)_2$. This substance, which is also formed when an aqueous solution of platodipyridine bromide is allowed to remain, or boiled with hydrobromic acid, forms needles, or yellow aggregates of microscopic needles; it is insoluble in water, and nearly so in aqueous ammonia. As in the case of the analogous chlorine compound, small quantities of an isomeric compound, $PtBr_2(C_5NH_5)_2$, were also obtained.

Attempts to see if the carbonyl group in these compounds will react with hydroxylamine or phenylhydrazine, as it does in ketones and aldehydes, gave negative results. Hydroxylamine exercises a reducing action. With an acetic acid solution of phenylhydrazine, carbonyl chloroplatinite yields an unstable *phenylhydrazine carbonyl chloroplatinite*, $COPtCl_2,C_6H_5N_2H_3$, which crystallises from ethyl acetate in yellow plates. It is decomposed by hot hydrochloric acid, but dissolves in a hot hydrochloric acid solution of carbonyl chloroplatinite, and, on cooling the solution, the *hydrochloride*,

$$COPtCl_2,C_6H_5N_2H_3,HCl,$$

separates out in orange-yellow needles, soluble in alcohol and ethyl acetate, but not in benzene, carbon bisulphide, or ether; it is decomposed by water when heated at 100°. C. F. B.

Action of Bromine on Para- and Ortho-hydroxyquinoline. By A. Claus and H. Howitz (*J. pr. Chem.* [2], **44**, 433—451).—4 : 3-*Bromhydroxyquinoline hydrobromide* separates as a yellow, crystalline precipitate when bromine (1 mol.) is added to a solution of 3-hydroxyquinoline in 10—12 times its weight of glacial acetic acid. It is sparingly soluble in cold water, and crystallises from hot water in small, hard, lustrous granules. It has no definite melting point, but dissociates when heated. When the aqueous solution of the hydrobromide is decomposed by potassium hydroxide or ammonia, and acidified with acetic acid, 4 : 3-*bromhydroxyquinoline* is precipitated in felted, small, slender needles; it melts at 186° (uncorr.), and sublimes; the *platinochloride*, with 2 mols. H_2O, is described. By oxidation with permanganate, the base yielded pyridinedicarboxylic acid, which was converted into nicotinic acid (m. p. 227—229°) when heated; this is evidence that the bromine atom is not in the pyridine ring. The orientation given is also supported by the fact that this bromhydroxyquinoline is one of the products of the quinolisation of metabromoparahydroxaniline by Skraup's method, as will be shown

in a future memoir. The hydrobromide is also formed when a solution of bromine in chloroform is added to one of 3-hydroxyquinoline in the same solvent. But an intensely reddish-yellow precipitate is formed when the reaction takes place in a solution in concentrated hydrobromic acid, or when bromine is added to a solution of 3-hydroxyquinoline in chloroform; this compound would appear to contain more hydrogen bromide than the yellow hydrobromide, into which it changes, after a time, with evolution of hydrogen bromide.

When bromine (1 mol.) acts on 1-hydroxyquinoline, a mixture of the hydrobromides of the unaltered base, and of bromo- and dibromo-1-hydroxyquinoline is formed. The product is boiled with water, and the solution, either before or after filtration, mixed with sodium acetate; the precipitate is dissolved in hydrochloric acid, and again precipitated by sodium acetate. The bases are next dissolved in hydrochloric acid, and the solution mixed with sufficient water to render it turbid; after some hours, the dibromo-derivative separates, and is treated by the same process several times to purify it. The bromo-derivative can be obtained pure from the solution after a very small quantity of sodium acetate has been added to precipitate the remaining dibromo-derivative. The two can also be separated by fractional distillation with steam, when the bromo-derivative passes over first.

4 : 1-*Bromhydroxyquinoline* crystallises from hot water in small, colourless needles, melts at 124° (uncorr.), sublimes in various but ill-defined forms, and is practically insoluble in cold water. The *platinochloride* was obtained. When oxidised by permanganate, the base yields non-brominated pyridinedicarboxylic acid; this settles its orientation.

4 : 3 : 1-*Dibromhydroxyquinoline* crystallises in lustrous, slender, yellowish needles, melts at 196° (uncorr.), sublimes in colourless needles when heated, and dissolves easily in chloroform, acetone, benzene, glacial acetic acid, and alcohol, but only sparingly in ether, and not at all in cold water. When oxidised by permanganate, it yields pyridinedicarboxylic acid; this shows that the bromine atoms are not in the pyridine ring. When the hydrobromide is suspended in chloroform and acted on by bromine, a red additive compound is produced, which easily decomposes, like that described above.

A. G. B.

Oxidation of Piperidine and Tetrahydroquinoline Derivatives. By C. Schotten and W. Schlömann (*Ber.*, **24**, 3687—3700). —Picrylpiperidine (compare Turpin, Trans., 1891, 714) is hardly acted on at all by potassium permanganate, even on long-continued heating; on oxidation with nitric acid or chromic acid, it yields resinous products.

Phenylsulphone-δ-amidovaleric acid, $SO_2Ph{\cdot}NH{\cdot}[CH_2]_4{\cdot}COOH$, is obtained, together with small quantities of phenylsulphonamide, when phenylsulphonepiperidine (compare Hinsberg, this vol., p. 64) is oxidised with potassium permanganate. It crystallises from hot water in colourless, nacreous plates, melts at 97°, and is readily soluble in alcohol, ether, glacial acetic acid, and light petroleum, but only sparingly in benzene and chloroform; when boiled with acetic anhydride, it is converted into a crystalline anhydride. The *barium* salt

$(C_{11}H_{14}O_4NS)_2Ba$, *zinc* salt, with $2H_2O$, and *copper* salt (anhydrous) were prepared. The *silver* salt, $C_{11}H_{14}O_4NSAg$, crystallises in lustrous plates. When the acid is heated with concentrated hydrochloric acid at 180°, it yields δ-amidovaleric acid phenylsulphonate,

$$C_5H_{11}NO_2,C_6H_5\cdot SO_3H;$$

this salt begins to melt at about 105°, and is not completely liquefied until the temperature has risen to 145°; when, after it has solidified, the same portion is again heated, it melts quite sharply at 107°. When phenylsulphone-δ-amidovaleric acid is heated with concentrated hydrochloric acid and barium chloride at 250°, it seems to be decomposed into δ-amidovaleric acid, sulphuric acid, and benzene.

Phenylsulphonetetrahydroquinoline, $C_9NH_{10}\cdot SO_2Ph$, prepared by shaking tetrahydroquinoline with potash and phenylsulphonic chloride, crystallises from dilute alcohol in large, colourless plates, melts at 67°, and is volatile with steam; it is readily soluble in benzene and chloroform, but more sparingly in glacial acetic acid, ether, alcohol, and light petroleum, and insoluble in water. On oxidation with potassium permanganate, it yields very small quantities of an acid, the nature of which was not determined, and a little phenylsulphonamide; with fuming nitric acid, it yields a yellow compound which is insoluble in soda.

Methyl tetrahydroquinolinecarboxylate, $C_9NH_{10}\cdot COOMe$, is obtained when tetrahydroquinoline is treated with methyl chlorocarbonate in the cold. It melts at about 35°, and is insoluble in water, alkalis, and acids, but soluble in the ordinary organic solvents; on oxidation with boiling potassium permanganate, it gives a substance which crystallises in red needles, melts at 175°, and gives the indophenin reaction; when heated with potassium permanganate in the cold, it yields very small quantities of an acid which melts at 155—156°. The *dinitro*-derivative, $C_{11}H_{11}N_3O_6$, prepared by dissolving methyl tetrahydroquinolinecarboxylate in fuming nitric acid, crystallises from alcohol in golden needles, melts at 174° with decomposition, and is not decomposed by boiling alkalis or acids; it is insoluble in ether and light petroleum, and only sparingly soluble in alcohol, but readily in benzene.

F. S. K.

Synthesis of Phenylpyrazolidine. By A. Michaelis and O. Lampe (*Ber.*, **24**, 3738—3740).—Sodium phenylhydrazine (2 mols.), benzene, and trimethylene bromide (1 mol.) are mixed and allowed to remain for some time at the ordinary temperature, the reaction being completed by heating on the water-bath; the benzene solution is treated several times with water, and finally with dilute hydrochloric acid; the acid solution, after neutralisation with alkali, is extracted with ether. After the ether is distilled, and the residue fractionated, *phenylpyrazolidine*, $NPh<\begin{matrix}CH_2\cdot CH_2\\ |\\ NH\cdot CH_2\end{matrix}$, is obtained as a colourless, or pale-yellow, liquid with a faint, characteristic odour; it boils at 210° under a pressure of 165 mm., and at 160° under a pressure of 20 mm. The compound has well marked basic properties, reduces alkaline copper solutions on warming, and is readily oxidised either by exposure to air or on treatment with mercuric oxide,

forming phenylpyrazoline. The picrate crystallises in short, yellow needles. The above synthesis probably proceeds in two stages, an intermediate compound, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NPh{\cdot}NH_2$, being first formed; this is then condensed by the excess of sodium phenylhydrazine; the reaction is therefore analogous to the formation of pyrrolidine from δ-chlorobutylamine by the action of alkalis.

A technical product, termed "phenylpyrazine," which is formed by the action of ethyl β-bromopropionate on phenylhydrazine in alkaline solution, is 1 : 5-phenylpyrazolidone, $NPh<\begin{matrix}CO\cdot CH_2\\ |\\ NH\cdot CH_2\end{matrix}$. The compound $C_9H_8N_2O_2$, prepared by Michaelis and Burmeister from ethyl chloromalonate and phenylhydrazine (compare Abstr., 1891, 1068), proves to be 1 : 3 : 5-phenylpyrazolidone, $NPh<\begin{matrix}CO\cdot CH_2\\ |\\ NH\cdot CH_2\end{matrix}$. J. B. T.

The Osazone of Hydroxypyruvic Acid. By W. Will (*Ber.*, **24**, 3831—3834).—In a previous paper (Abstr., 1891, 542), the author described a substance obtained by the action of hydrogen chloride on an alcoholic solution of the osazone of hydroxypyruvic acid, which he regarded as its ethyl salt. After dissolving in alkali and reprecipitating with acid several times, and finally recrystallising from alcohol, it is obtained in reddish-yellow aggregates of needles, which, from the analysis and molecular weight determination, have the composition $C_{15}H_{12}N_4O$. It is therefore not the ethyl salt, as formerly supposed, but is obtained from the osazone by loss of the elements of water, and is identical with the phenylhydrazineketophenylpyrazolone obtained by Knorr by heating the osazone with acetic anhydride (Abstr., 1888, 724). Its formation is represented as follows:—

$$N_2HPh{:}C<\begin{matrix}COOH\\ CH{:}N{\cdot}NHPh\end{matrix} = N_2HPh{:}C<\begin{matrix}CO{\cdot}NPh\\ |\\ CN{:}N\end{matrix} + H_2O.$$

It is insoluble in water, readily soluble in alcohol and ether, sublimes in small quantities, and colours wool and silk yellow in alkaline solution.

The osazone of hydroxypyruvic acid differs from the similar compounds investigated by Knorr, inasmuch as the solutions of its salts do not yield the pyrazolone directly on acidification. The osazone itself yields a sodium salt, as already found by Nastvogel (Abstr., 1889, 237). The pyrazolone, however, also yields a *sodium compound*, which crystallises in slender, yellow needles, and melts at about 300° with decomposition. It also forms a *silver compound*, $C_{15}H_{11}AgN_4O$, which crystallises in reddish-yellow plates, becomes brown at 206°, and melts at 215°.

The ethyl salt of the osazone may be obtained by the action of methyl iodide and alkali on its alcoholic solution. It is a yellow, microcrystalline powder which melts at 222—223°, and is insoluble in alkalis and dilute acids. H. G. C.

Phenylguanazole. By G. Pellizzari (*Gazzetta*, **21**, ii, 141—154). —*Phenylguanazole* is prepared by heating a mixture of dry dicyano-

diamide with phenylhydrazine hydrochloride, in molecular proportion, at 150°; much ammonia is evolved during the reaction, and, as spontaneous heating occurs, the mixture must be cooled if the temperature rises above 180°. The vitreous, yellow product is crystallised from dilute hydrochloric acid, dissolved in water, and decomposed by concentrated caustic potash, when the base separates in red needles; on recrystallisation from alcohol, it is obtained in large, hard, slightly yellowish crystals melting at 174—175°. It is very soluble in alcohol and water, but only sparingly in chloroform, ether, or benzene; it is precipitated from its aqueous solutions by caustic soda and caustic potash. The molecular formula, as determined by the cryoscopic method, is $C_8H_9N_5$. The aqueous solution is neutral to test-paper. The *hydrochloride*, $C_8H_9N_5,HCl$, crystallises in thin, white scales, very soluble in water and alcohol, and melts at 240°. The *platinochloride*, $(C_8H_9N_5)_2,H_2PtCl_6$, forms yellow, prismatic needles. The aqueous solution of the base gives a white, flocculent precipitate with silver nitrate, soluble in hot water, nitric acid, and ammonia; it is a molecular compound of phenylguanazole with silver nitrate,

$$C_8H_9N_5,AgNO_3.$$

Silver sulphate and mercuric chloride give white precipitates with aqueous solutions of the base; mercurous nitrate gives a white precipitate soon turning yellow; and copper salts give a yellowish-green precipitate. These precipitates are all molecular compounds. The reaction between dicyanodiamide and phenylhydrazine hydrochloride may be carried out in alcoholic solution by heating for eight hours in a closed tube at 100°. The reaction is represented by the equation

$$NHPh\cdot NH_2 + NH\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH_2 = \begin{matrix} C(:NH)\cdot NH \\ | \\ NH\cdot C(:NH) \end{matrix}\!\!>NPh + NH_3.$$

Anilbiguanidine is probably an intermediate product of the reaction, for if anilguanidine hydrochloride (1 part) and cyanamide (1 part) be boiled with water (8 parts) for six hours, and treated with potash, ammonia is evolved and phenylguanazole separates. Phenylguanazole is also obtained by heating together at about 160° equal parts of anilguanidine hydrochloride and guanidine carbonate; large quantities of ammonia are evolved; the product is dissolved in dilute hydrochloric acid, and filtered; on treating with solid potash, crude phenylguanazole separates, and is purified by repeated extraction with chloroform. A mixture of biguanide with phenylhydrazine in molecular proportion, when heated at 120—160°, evolves much ammonia, and, on extracting the product with alcohol, evaporating, dissolving in water, treating with a little potash, filtering, and adding excess of potash, phenylguanazole is obtained. The yield by the last two methods is small, but they show the very great analogy which exists between phenylguanazole and phenylurazole (Trans., 1888, 550).

Ethylanilbiguanidine, $NH_2\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH\cdot NEtPh$, is prepared by heating unsymmetrical ethylphenylhydrazine hydrochloride with dicyanodiamide in molecular proportion, at 160—170°, for half

an hour. No ammonia is evolved. The product is dissolved in water, filtered, and treated with caustic potash; the base separates as an oil which is extracted by agitation with ether, and the residue left on evaporating the ethereal solution is boiled for some time with water to eliminate unaltered ethylphenylhydrazine; caustic potash is then added, and the precipitate again extracted with ether; on evaporating the ether, the base is obtained as a vitreous, friable mass which softens at about 50°. It is very soluble in alcohol, ether, and benzene, less so in water; it has a strongly alkaline reaction, and absorbs carbonic anhydride. When boiled with potash, it yields ammonia and ethylphenylhydrazine. The *sulphate*, $C_{10}H_{16}N_6,H_2SO_4$, is obtained in small, colourless crystals which are very soluble in water, but only sparingly in alcohol. W. J. P.

Tropine. By G. Merling (*Ber.*, **24**, 3108—3126).—The experiments to be described, taken in conjunction with the facts already known, prove that neither the formula proposed by the author, nor that of Ladenburg, which Liebermann has already shown to be untenable (Abstr., 1891, 749), represents the constitution of this compound. In the present research, the author commenced his experiments with Roth's methyltropidine (Abstr., 1884, 761), a compound which proves to have properties entirely different from those ascribed to it by Roth, and proceeded on the lines laid down by him for the investigation of certain bases allied to piperidine (*Annalen*, **264**, 310; Abstr., 1891, 1506).

α-Methyltropidine ($\Delta^{3:5}$-*dihydrobenzyldimethylamine*, see below), $C_6H_7\cdot CH_2NMe_2$, is prepared by distilling a dilute aqueous solution of tropidinemethylammonium hydroxide until it reaches a concentration of 1 : 10, and then driving the base over with a current of steam; it is a colourless, mobile oil, of a faint ammoniacal odour, and cannot be distilled, as it changes into β-methyltropidine on heating; the yield is equal to that of the tropidine employed. The *platinochloride*, $(C_9H_{15}N)_2,H_2PtCl_6$, crystallises from boiling water in orange-yellow prisms, and melts at 173—174°; the *aurochloride*,

$$C_9H_{15}N,HAuCl_4,$$

is a golden-yellow, crystalline precipitate sparingly soluble in water, and decomposing when boiled with it; the *methiodide*, $C_6H_9NMe_3I$, is readily soluble in hot water, sparingly in cold, and melts at 162° with the evolution of gas. *Hydrochloro-α-methyltropidine*,

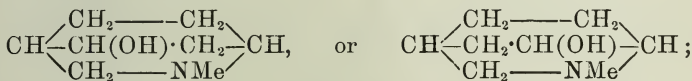
$$C_6H_7HCl\cdot CH_2\cdot NMe_2,$$

is obtained as the hydrochloride, when α-methyltropidine is allowed to remain for some days at the ordinary temperature with a solution of hydrogen chloride saturated at 0°; the *aurochloride*,

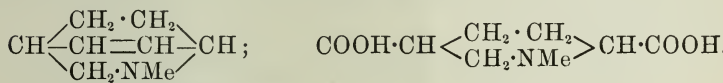
$$C_9H_{16}ClN,HAuCl_4,$$

separates as a yellow, crystalline precipitate on adding auric chloride, and the free base as a colourless, mobile oil on adding sodium hydroxide to the solution; the latter changes slowly at the ordinary temperature, or quickly at the temperature of the water-bath, into a

viscid syrup which consists essentially of tropidinemethylammonium chloride. It is poured into water and distilled in a current of steam, when a small quantity of α-methylpiperidine passes over; the residue is shaken with ether to remove the resinous substances, solutions of sodium hydroxide and potassium iodide added, and the precipitated tropidinemethylammonium iodide crystallised from boiling alcohol; it is next converted into the chloride by silver chloride, and this salt yields tropidine and methyl chloride on dry distillation. These reactions are analogous to the conversion of pentallylcarbindimethylamine into methyl-α-pipecoline, and indicate the presence of the group $\vdots C\cdot NMe\cdot CH(CH_2R')-$ in tropidine. The formation of α-ethylpyridine from norhydrotropidine (Ladenburg) shows that the α-carbon atom carries an atom of carbon not belonging to the hydrogenised pyridine nucleus; whilst that of the bibasic tropic acid, by the oxidation of tropine with chromic acid, proves that the second carbon atom of the side chain is also in combination with one of the nuclear carbon atoms. When α-methyltropidinemethylammonium iodide is converted into the hydroxide, and this is boiled with water, it decomposes into tropilidene, C_7H_8, trimethylamine, and water, a reaction which points to the presence of the group $=CH\cdot CH_2\cdot NMe_2$ in α-methyltropidine. These facts are only to be accounted for by adopting the following formulæ:—



Tropine.

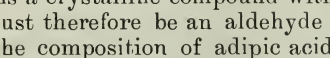


Tropidine. Tropic acid.

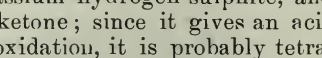
Methyltropine is, therefore, Δ^3-hydroxytetrahydrobenzyldimethylamine, and α-methyltropidine is $\Delta^{3:5}$-dihydrobenzyldimethylamine. Tropilidene, C_7H_8, when dissolved in carbon bisulphide and treated with bromine, forms a *dibromide* which is an oil miscible with ether and having a camphor-like odour; when kept in a desiccator, it resinifies by degrees, and, when heated on the water-bath for some hours, hydrogen bromide is evolved, and it is converted into a crystalline mixture of benzyl bromide and a substance separating from alcohol in yellow tablets, which is perhaps an isomeride of the dibromide. When tropilidene (1 gram) is heated in a reflux apparatus for an hour with sulphuric acid (5 grams), water (20 grams), and potassium dichromate (3·2 grams), a mixture of benzoic acid and benzaldehyde is formed with evolution of carbonic anhydride. Tropilidene is, therefore, probably $CH_2{:}C<\begin{matrix}CH_2{\cdot}CH_2\\ CH-CH\end{matrix}>CH$.

β-Methyltropidine, $C_7H_9NMe_2$, is prepared as follows:—α-Methyltropidine is heated at 140—150° in a reflux apparatus; on now removing the source of heat, the temperature rises to 190°; the liquid is maintained at this for some minutes, and is then distilled, when

small quantities of di- and tri-methylamine pass over, and at 200° a few drops of tropylen; whilst β methyltropidine passes over at 204—205° (757 mm.), and a small quantity of a base boiling at a very high temperature remains behind as a thick, brown oil. It is a colourless, highly refractive oil, having a characteristic odour, and a sp. gr. 0·922 at 15°. When β-methyltropidine is dissolved in hydrochloric acid and the solution heated, tropylen separates as an oil and is driven over with a current of steam; whilst dimethylamine hydrochloride remains behind. The fact that Ladenburg obtained tropylen and dimethylamine by heating tropidine methiodide with potash is, therefore, explained as follows:—α-Methyltropidine is initially formed, and this changes into the β-compound, which then decomposes into tropylen and dimethylamine. When β-methyltropidine and methyl iodide are mixed in molecular proportion in methyl alcoholic solution, tetramethylammonium iodide separates: the quicker if heat is applied; whilst after removing the iodine from the solution by silver chloride, platinic chloride precipitates a *platinochloride*, $(C_7H_7Me)_2,H_2PtCl_6$, as a bright-yellow, amorphous precipitate, and on evaporating the filtrate, an oily compound at first separates, and, later, lustrous crystals of the *platinochloride*, $C_7H_7Me_3,H_2PtCl_6$. The author finds, contrary to Ladenburg's statement, that tropylen forms a crystalline compound with potassium hydrogen sulphite, and it must therefore be an aldehyde or a ketone; since it gives an acid of the composition of adipic acid on oxidation, it is probably tetrahydrobenzaldehyde, and in concordance with the above formulæ, the Δ^3-derivative. Ecgonine and anhydroecgonine must, in conformity with the above-given formulæ for tropine and tropidine, be represented as follows:—



Ecgonine.



Anhydroecgonine.

The formation of dihydrobenzaldehyde from dibromanhydroecgonine (Eichengrün and Einhorn, Abstr., 1891, 65), then, admits of simple explanation. The dihydrobenzaldehyde must be the $\Delta^{3:5}$-derivative. A. R. L.

A Violet from Codeïne. By P. Cazeneuve (*Compt. rend.*, **113**, 747—749).—10 grams of codeïne is heated with 10 grams of paranitrosodimethylaniline in presence of a litre of ethyl alcohol of 93° for 300 hours. When the liquid cools, it deposits tetramethyldiamidoazobenzene. The alcohol is distilled off and the residue boiled with water; after cooling, the liquid is filtered and agitated with amyl alcohol, which dissolves out the violet colouring matter, whilst a beautiful blue colouring matter remains in the water. When the amyl alcohol is evaporated, the violet compound separates in amorphous, lustrous flakes, somewhat soluble in water, but especially soluble in alcohols and in ether, forming dichroic solutions. When the aqueous solution is poured on to strong sulphuric acid, it gives, like the safranines, a green zone, changing to blue, and then to violet,

which indicates the presence of poly-acid combinations. The morphine violet gives a similar reaction.

Codeïne violet dyes silk, wool, and gun-cotton directly, but the colour alters somewhat when exposed to light.

When the amyl alcohol solution of the compound is mixed with alcohol and ether, and treated with platinic chloride, a platinochloride is obtained with a paler colour than the platinochloride of the analogous morphine compound. It has the composition

$$NMe_2{\cdot}C_6H_4{\cdot}N{:}C_{17}H_{18}MeNO_4,H_2PtCl_6,$$

and hence codeïne violet has the composition

$$NMe_2{\cdot}C_6H_4{\cdot}N{:}C_{17}H_{18}MeNO_4.$$

The yield is small, but better results were not obtained by varying the proportions of the reacting substances. Heating in a sealed tube gave a smaller yield (compare Abstr., 1891, 1220).

C. H. B.

An Alkaloïd from Javan Coca Leaves. By F. Giesel (*Chem. Centr.*, 1891, ii, 488, from *Pharm. Zeit.*, **36**, 419—420).—From 20 kilos. of a small-leaved Javan coca, the author obtained 1 kilo. of cinnamylcocaïne, whilst about three times this amount, besides some cocaïne, remained uncrystallisable. From the mother liquors an alkaloïd was separated as hydrobromide, which resembled dextrococaïne. The *hydrobromide* melted at 49°.

The hydrochloride is more readily soluble in water, and less soluble in alcohol, than is the hydrochloride of dextrococaïne. The salts of the new alkaloïd are precipitated crystalline from quite dilute solutions by potassium dichromate, which is not the case with the salts of cocaïne or dextrococaïne; moreover, the polarised ray is not perceptibly deviated.

Concentrated hydrochloric acid splits it up into benzoic acid and ecgonine hydrochloride, without the formation of an intermediate product, as in the case of dextrococaïne.

The alkaloïd could not be detected in the leaves of American truxillo; at the same time, an alkaloïd, somewhat resembling Hesse's hygrine, but different from it, was obtained from them. It differs from Hesse's hygrine in its solubility in solutions of the alkalis, and is destroyed by potassium permanganate; whilst Hesse's remains unchanged. It occurs in the leaves in quantities up to 0·2 per cent, and is a constituent of the plant, and not a product of decomposition.

J. W. L.

Cyanmethæmoglobin and Detection of Hydrogen Cyanide. By R. Kobert (*Chem. Centr.*, 1891, ii, 591, from *Apoth. Zeit.*, **6**, 386).—Researches carried out by the author indicate that hydrogen cyanide forms with methæmoglobin a red compound *cyanomethæmoglobin*, which differs from oxyhæmoglobin and its modifications in that its spectrum is not characterised specially by any band. The remarkably bright-red colour of the blood, after poisoning with hydrogen cyanide, in places where the formation of methæmoglobin

has taken place, is caused by the formation of the cyanogen compound.

Blood which contains the cyanogen compound may be detected thus:—1 c.c. of the blood is diluted with 99 c.c. of water and a 1 per cent. solution of potassium ferricyanide is added drop by drop. If cyanogen is absent, the colour of the solution passes from red to yellow, owing to the formation of methæmoglobin, and it shows the corresponding spectrum. In the presence of cyanogen, the colour only becomes brighter red, and shows no absorption band. Hydrogen cyanide may be detected by means of this test. Healthy blood is employed, and, after diluting with water (1 c.c. of blood to 99 c.c. of water), it is shaken with a small crystal of potassium ferricyanide until the red colour has just changed to yellow, and a little of the liquid under investigation is poured on to the surface. The presence of hydrogen cyanide causes a bright-red coloration to form. The solutions must not be alkaline, but should be just acid.

If blood contains cyanogen, a 1 per cent. solution retains its colour for some time; whereas healthy blood becomes darker at the end of a few hours or days, and shows the spectrum of hæmoglobin.

J. W. L.

Transformations of Albumins. By G. Patein (*Compt. rend. Soc. Biol.*, 1891, 207—212).—From experiments on egg-albumin and serum-albumin, it is shown that the action of acetic acid and alkalis produces changes in the albumin which render it no longer coagulable by heat or precipitable by certain reagents. The same sometimes occurs in the albumin which passes into the urine in cases of disease.

W. D. H.

Physiological Chemistry.

Digestive Ferments in Crustacean Eggs. By J. E. Abelous and F. Heim (*Compt. rend. Soc. Biol.*, 1891, 273—275).—Various crustacean eggs were found to contain an amylolytic, an inverting, and a tryptic ferment. Their amount and activity probably varies with the degree of maturity of the eggs. These are regarded as enzymes, not as organised ferments. W. D. H.

Formation of Sugar in the Organism when Oxygen is deficient. By A. Dastre (*Compt. rend. Soc. Biol.*, 1891, 681—684). —The recent experiments of Araki (Abstr., 1891, 1125—1392) and by Zillessen (*ibid.*, 1126) are merely confirmatory of some of a more com-

plete nature made by the author some years ago (*Glycémie asphyxique*, 1879); these are not alluded to by the authors just mentioned.

W. D. H.

Gases of Peptone Blood. By Blachstein (*Arch. f. Anat. u. Physiol., Physiol. Abth.*, 1891, 394—401).—In dogs, Labousse (Abstr., 1889, 531) has shown that injection of "peptone" lessens the amount of carbonic anhydride in the blood, whilst the oxygen remains normal, or rather over the normal. It is now shown that in the rabbit, an animal whose blood is not rendered incoagulable by peptone, the same change in the blood gases occurs. Moreover, the amount of carbonic anhydride in the lymph is not lessened, and so the diminution is not explicable on the ground of lessened metabolism. W. D. H.

The Specific Gravity of the Blood of Europeans living in the Tropics. By M. Glogner (*Virchow's Archiv*, **126**, 109—113).—The specific gravity of the blood was estimated by Hammerschlag's method. A drop of blood is placed in a mixture of benzene and chloroform, and then benzene or alcohol, as the case may be, is added until the drop of blood swims. The mixture is filtered through linen, and its specific gravity, taken with the hydrometer, gives that of the blood.

The persons, 20 in number, on whom the observations were made were Europeans who had lived for varying periods in the East India Islands (six months to 29 years), and were suffering from varying degrees of "tropical anæmia." The average number of corpuscles was found to be normal; but the sp. gr was 1·053 instead of the normal 1·062. The anæmia thus appears to be due to loss in the constituents (probably proteïds) dissolved in the blood plasma. W. D. H.

Tropical Anæmia. By C. Eijkman (*Virchow's Archiv*, **126**, 113—124).—This investigation resembles that in the preceding abstract, but is rather more extensive. The specific gravity of blood was estimated by Schmaltz' capillary pycnometer (*Arch. Klin. Med.*, 1890); the corpuscular richness by counting; the percentage of hæmoglobin by Fleischl's hæmometer. Observations were made both on Malays and Europeans, the latter being classified according to their length of residence in the tropics. The blood on the average gave throughout practically the same number of corpuscles, and the same percentage of hæmoglobin. The average specific gravity was 1·057, length of stay in the Indies making no difference. Schmaltz gives the normal specific gravity as 1·059; so there is a slight fall, but nothing like so great as in the more familiar forms of anæmia. W. D. H.

Disappearance of Sugar from the Blood. By V. Harley (*J. Physiol.*, **12**, 391—408).—In view of Schenk's statement (Abstr., 1891, 350, 504) that a considerable amount of sugar is lost when it is estimated in albuminous mixtures such as serum, a number of investigations were made on this subject. A known amount of dextrose was mixed with defibrinated calf's blood, the proteïds removed by acetic acid, heat, and filtration, and the sugar estimated in the filtrate and washings; the loss varied from 0 to 4·8 per cent. The reason of the

variation appears to be the behaviour of the proteïd on heat coagulation; if the coagulum formed is dense and firm, the loss of sugar is great. If the proteïd separates in loose, flocculent curds, the precipitate is more readily washed, and the loss of sugar reduced to a minimum.

Similar results followed experiments made with blood drawn directly from an artery in a living animal, and also when other methods of precipitating the proteïds (potassio-mercuric iodide, mercuric chloride) were employed; and the general conclusion is drawn that the loss of sugar is due to mechanical retention by, not chemical combination with, the coagulated proteïd. In addition to this, however, the element of time has to be taken into account; the longer the blood, if fresh, and sugar solutions are mixed, the greater is the loss of the sugar; this is not due to bacteria. The glycolysis is of a progressive character. W. D. H.

Glycolytic Power of Blood and Artificial Production of Diabetes. By R. Lépine and Barral (*Compt. rend.*, **113**, 729—730).—Moderate bleeding of a dog at first (after a short time) increases the glycolytic power of the blood, but repeated bleeding reduces it. Ligature of Wirsung's canal causes a great increase of the glycolytic power of the blood. Grützner found that under the same conditions there was an increase in the saccharifying power of the urine, and the authors find that this is true also of the blood. Section of the nerves of the pancreas is followed by a great increase in the glycolytic and saccharifying power of the blood. Electrification of the lower end of the pancreatic nerves produces diabetes after a short time.

C. H. B.

Influence of Muscular Work on the Elimination of Creatinine. By J. Moitessier (*Compt. rend. Soc. Biol.*, 1891, 573—574).—After muscular work (walking), no increase in the amount of creatinine in the urine was observed. The experiments were made on the author's own person. W. D. H.

Xanthocreatinine in the Urine. By G. Colosanti (*Gazzetta*, **21**, ii, 188—192).—The urine of the lion is very rich in urea, which, when extracted by Hoppe-Seyler's method, crystallises in thin, snow-white scales, not in needles as does that obtained from the urine of the dog. The alcoholic mother liquor from the crystallisation and washing of the urea when concentrated is of a syrupy consistency, and has an aromatic odour; it contains, besides much creatinine, xanthocreatinine, which may be separated as a yellow, crystalline powder.

Monari (Abstr., 1886, 613) has shown that if large quantities of creatine, or creatinine, are introduced into the circulation, either by intravascular injection or as the result of excessive muscular effort, the bases are partly eliminated as xanthocreatinine. As the rich meat diet of the lion introduces into the system large quantities of creatine, the author supposes that part of the base is secreted as xanthocreatinine. W. J. P.

Is Alcohol Eliminated by the Milk? By F. Klingemann (*Virchow's Archiv*, **126**, 72—80).—By administering fairly large doses of alcoholic liquors to nursing women, none was ever found in the milk. In animals in which proportionally larger doses were given, minute traces were occasionally found. W. D. H.

Action of Pilocarpine on the Excretion of Milk. By C. Cornevin (*Compt. rend. Soc. Biol.*, 1891, 628—630).—Pilocarpine is a drug which increases the amount of many secretions, such as sweat and saliva. By experiments on cows, it was, however, found that it does not increase the amount of milk secreted. Analysis of the milk showed a slight increase in the amount of lactose. There is no glycosuria. W. D. H.

Excretion of Uric Acid and Urea. By W. P. Herringham and H. O. Davies (*J. Physiol.*, **12**, 475—477).—Haig states that the proportion of uric acid to urea varies inversely with the daily total acidity of the urine. Haig estimated uric acid by Haycraft's method. In the present research, uric acid was estimated by Ludwig's modification of Salkowski's process, and urea by the hypobromite method. Two experiments were made, one of 16 days on a mixed diet, one of eight days on a vegetable diet. The proportion of uric acid to urea varied, but bore no fixed relation to the total acidity of the urine. W. D. H.

Excretion of Uric Acid, Urea, and Ammonia. By W. P. Herringham and E. W. Groves (*J. Physiol.*, **12**, 478—484.)—A series of experiments similar to the preceding, but performed more carefully, the composition of the diet being noted. The results obtained showed that the excretion of uric acid does not vary inversely with the daily acidity of the urine, and that uric acid may be passed to the amount of $\frac{1}{24}$th of the urea without bad effects. On three occasions sodium salicylate was given; these coincided with large excretions of uric acid. This may, however, have been due to the salicyluric acid in the urine; or it may have been accidental, as on other days, when no drug was given, the excretion was as large. W. D. H.

Heat Production in Nerves during Excitation. By G. N. Stewart (*J. Physiol.*, **12**, 409—425).—In the nerves of rabbits and dogs there is not even a rise of temperature of the general nerve sheath of $\frac{1}{2000}$th of a degree during excitation. On theoretical grounds, the statement of Rolleston (Abstr., 1890, 536), that a frog's nerve gives off heat when it dies, is considered to be erroneous. W. D. H.

Physiological Action of Nickel Carbon Oxide. By M. Hanriot and C. Richet (*Compt. rend. Soc. Biol.*, 1891, 185—186).—This compound is extremely poisonous. The blood shows the spectrum of carbonic oxide hæmoglobin. (Compare McKendrick and Snodgrass, Abstr., 1891, 1130.) W. D. H.

Physiological Action of Nickel Carbon Oxide. By P. Langlois (*Compt. rend. Soc. Biol.*, 1891, 212—213).—The oxygen of

oxyhæmoglobin is displaced by this substance, but it is regarded as unsettled whether the compound formed is carbonic oxide hæmoglobin, or hæmoglobin united to the nickel compound.

W. D. H.

Physiological Action of Trimethylamine. By Combemale and Brunelle (*Compt. rend. Soc. Biol.*, 1891, 175—178).—Inhalation of the vapour of trimethylamine produces an increased secretion of saliva. The same effect follows its administration by the mouth, or under the skin. The alkalinity of the saliva is greater than normal. Occasionally vomiting is produced, also increase of the nasal mucus and of tears. There is always slight albuminuria. After subcutaneous administration, there is local inflammation at the point of injection, leaving a wound which takes a long time to heal. A dose of 3 centigrams per kilo. of body weight causes a lowering of body temperature. W. D. H.

Physiological Action of Dinitrobenzene. By A. Huber (*Virchow's Archiv*, **126**, 240—270).—The main effects of dinitrobenzene, as tested on both cold- and warm-blooded animals, are changes in the blood, paralysis, and intense dyspnœa. The blood becomes of a dark chocolate colour; the red corpuscles are largely deprived of their pigment, which in frogs partly collects round the nucleus. Spectroscopic investigation showed an absorption band in the red, reminding one of the similar band of acid hæmatin, and of methæmoglobin, but not identical with either. It is spoken of as the dinitrobenzene band, and it is considered that this compound acts in a specific manner on the blood pigment. After large doses, the urine was found to be brown in colour, and to contain a strongly reducing substance, and sometimes dinitrobenzene was itself present. The body temperature is lowered. The illness which workers in roburite factories suffer from appears to be caused by dinitrobenzene fumes.

W. D. H.

Relation between the Chemical Constitution and Physiological Action of Compounds of the Aromatic Series. By G. Oddo (*Gazzetta*, **21**, ii, 237—258).—

Benzene Nucleus.—I. *Triazobenzene.*—This compound, prepared by the author's method (Abstr., 1891, 696), has a very energetic antipyretic and analgesic action on mammals, both in the normal and febrile conditions. Its antipyretic action is probably more powerful than that of any other known substance, the temperature in mammals falling almost to the point of collapse with complete anæsthesia; these effects last for 24 or more hours, paralysis and death often supervening. The action is accompanied by a rise in the pulse rate, and does not commence until some hours after administration, probably owing to its insolubility; the acidity of the stomach also affects the rapidity and extent of the action. It is probably eliminated from the body by the skin and lungs. Frogs, on the other hand, exhibit convulsive movements and depressed pulse. It thus appears that azoimide does not retain its physiological properties (*Ber.*, 1890, 1023; Abstr., 1891, 56 and 524) when in combination with organic radicles.

II. *Benzamide* acts as a gentle antipyretic; its action is rapidly developed, and soon ceases. It probably passes from the system through the skin and lungs.

Naphthalene Nucleus.—*Ethyl α-naphthylazoacetoacetate*,

$$C_{10}H_7{\cdot}N_2{\cdot}CHAc{\cdot}COOEt$$

(Abstr., 1891, 1381), gave negative results in experiments on dogs and frogs. *α-Acetonaphthalide*, which resembles some well-known antipyretics of the benzene group in constitution, likewise gave rise to no noteworthy symptoms. This behaviour is attributed by the author to the physiological inactivity of the naphthalene nucleus. The phenanthrene nucleus appears to be similarly inactive, a subcutaneous injection of 0·04 gram only feebly affecting a frog. In conclusion, the author ascribes the antipyretic properties of benzene compounds to the presence of the benzene nucleus, and regards the absence of these properties from naphthalene compounds as indicative of the absence of a preformed benzene nucleus from these substances and hence as confirmatory of Bamberger's centric formulæ.

S. B. A. A.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification of Organic Nitrogen. By T. Leone and O. Magnanini (*Gazzetta*, **21**, ii, 206—208).—The authors have instituted experiments to determine whether organic nitrogen is completely converted into nitric acid by the nitrifying organism. A quantity of gelatin solution containing 0·04—0·07 gram of nitrogen was dissolved in 2—3 litres of water, and kept at 32° for 45 days, after which time neither ammonia nor nitrous acid was present in the solution, so that the action may be considered to have ended. On determining the nitric acid, a deficit of 17·4—19·0 per cent. on the amount of nitrogen originally present was observed. This nitrogen must either have been evolved in the free state or remained in the solution as organic matter not convertible by the organism. W. J. P.

The Sources of the Nitrogen of our Leguminous Crops. By Sir J. B. Lawes and J. H. Gilbert (*Jour. Roy. Agri. Soc.* [3], **2**, 657—720).—Both the scientific interest and practical value of leguminous crops depend largely on the amount of nitrogen they contain and on the sources of this nitrogen; also on the great difference in these respects between them and the agricultural plants of other orders. Grain and root crops and potatoes cannot be successfully grown without the application of nitrogenous manure, whilst the direct effect of such manure is to increase not so much the nitrogenous as the non-nitrogenous constituents of the plants—the carbohydrates. This is well illustrated by the results of field experiments made at Rothamsted; the results show that when nitrogenous

manures are applied in conjunction with minerals, there is an enormous increase in the carbon assimilation and carbohydrates formed as compared with the amounts assimilated under the influence of minerals only. On the other hand, leguminous crops, grown without nitrogenous manure, contain a higher percentage of nitrogen than non-leguminous crops, and yield also a much greater amount of nitrogen over a given area of land; nitrogenous manures have little or no effect when given to them, and the carbon assimilation is not materially increased.

Boussingault's experiments, and the earlier experiments made at Rothamsted (this Journal, 1863, 100), showed that, under conditions of sterilisation and enclosure, there was no gain from free nitrogen in the growth of either *Gramineæ*, *Leguminosæ*, or other plants. The results obtained by Hellriegel and others, and especially those obtained at Rothamsted in 1888 (Abstr., 1890, 814), are next discussed. They show that, under non-sterilised conditions—in fact, with suitable microbe infection of the soil—there was nodule formation on the roots and considerable fixation of free nitrogen. These results have received confirmation from still more recent Rothamsted experiments, and also from the direct experiments of Schloesing, jun., and Laurent (Abstr., 1891, 353), who determined the loss of nitrogen which took place in the confined air in which their plants were grown.

In 1889, and since, quantitative experiments have been made with peas, beans, vetches, lupins, white clover, red clover, sanfoin, and lucerne; that is to say, with four annuals and four plants of longer life. The results, as far as they are available, show that without soil-extract seeding, and with no nodules, there was no gain of nitrogen; whilst with soil extract, and with nodule formation, there was a considerable gain of nitrogen, in fact, very many times as much nitrogen in the products of growth as in the seeds sown.

The difficulty at first experienced by Hellriegel in obtaining good results with lupins, and at Rothamsted with yellow and blue lupins in 1888, seems to be due to the infecting soil which was used being unsuitable. Nobbe's experiments (Abstr., 1891, 1533) indicate that there are a variety of leguminous nodule-organisms, which have very different effects with the different plants (compare also Beyerinck, Abstr., 1891, 1539). This would also be consistent with the observations made at Rothamsted with various plants, showing that the external appearance and distribution of the nodules were very different in the case of peas, vetches, lupins, and other plants.

A series of experiments was commenced at Rothamsted in 1890, with a view to the more detailed examination of the roots of the plants than was possible in the case of the strictly quantitative series. The plants were grown in pits, so arranged that some of the plants of each description could be taken up and their roots examined at three (or four) successive periods of growth. Each plant was grown in sand supplied with minerals and soil extract, and in a mixture of soil and sand. Generally speaking, in sand, the area of infection was limited, but the nodules were of great size; in soil with much greater distribution of the infecting organisms, there was a far greater number of nodules, which were, however, smaller than those grown in sand. The results of determinations of dry matter and nitrogen in

the nodules of the plants taken up at different periods indicate that in the case of the annual, when the seed is formed and the plant more or less exhausted, both the actual amount of nitrogen in the nodules and its percentage in the dry substance are greatly reduced; but that with the plant of longer life, although the earlier-formed nodules become exhausted, others are constantly produced, thus providing for future growth. And the results of these experiments, taken together with those of the quantitative series, show further an intimate connection between the gain of nitrogen by the *Leguminosæ* and the development of the nodules on their roots.

As to the manner in which nitrogen is fixed, it has been suggested that, under the conditions of the symbiosis, the plant is enabled to fix the free nitrogen of the atmosphere by its leaves; but there is little or nothing in the evidence we have which leads to this conclusion. It is also suggested that the bacteria of the nodules become distributed in the soil and there fix nitrogen, which is subsequently taken by the plants from the soil. In the Rothamsted experiments, however, no gain of nitrogen was observed in the soils. Berthelot found that soils both free from higher vegetation, and soils in which leguminous plants were growing, gained in nitrogen; and Schloesing, jun., and Laurent also found fixation to take place in soils under the influence of lower plants—lichens and algæ. Nevertheless, neither experience in practical agriculture, nor the nitrogen statistics of soils and crops, indicate any material fixation of free nitrogen under the agency of microbes within the soil, independently of leguminous growth. There is, however, evidence that, in soils and subsoils containing combined nitrogen, lower organisms may serve the higher by bringing the organic nitrogen into an available form. As examples may be mentioned the fungus of fairy rings, the fungus mantle observed by Frank on the roots of certain trees, and especially the nitrifying organisms. To return to the question of fixation, the most probable explanation seems to be that free nitrogen is fixed in the course of the development of the organisms within the nodules, and that the resulting nitrogenous compounds are absorbed and utilised by the plant. It may be mentioned that Loew (Abstr., 1890, 1052), viewing the question in the light of his own results with platinum in presence of alkali, suggested the possibility that the vegetable cell, with its active protoplasm, if in an alkaline condition, may fix free nitrogen with formation of ammonium nitrite. It was frequently found at Rothamsted that the contents of the nodules, when apparently in an active condition, showed a weak alkaline reaction.

Although much of the nitrogen of leguminous crops is sometimes obtained under the conditions described, from the free nitrogen of the air, a good deal is taken up from the subsoil, chiefly as nitric acid derived from the organic matter present in the soil. A difficulty in the way of the assumption that much of the greater assimilation of the Leguminosæ than by other plants is due to nitrification of the subsoil is the fact that the direct application of nitrates has but little effect on the growth of such plants. The two cases are, however, different—nitrates, when applied, percolate more or less alone through the soil, whilst nitrates formed as a result of action on the organic nitrogen

will probably be associated with other constituents liberated at the same time.

With regard to the more practical aspects of the subject, reference is made to the experiments of Schultz, of Lupitz, who has, for some years, grown leguminous crops over large areas of poor sandy soil, using kainite and phosphatic manures; he finds the lands thereby much benefited for subsequent cereal and other crops. The system is extending in other parts of Germany, and in this country Mr. Mason, of Eynsham Hall, Oxon, is making extensive experiments on the subject.

"The experimental results which have been brought forward clearly established that there is great gain of nitrogen under some conditions. It has also been clearly shown that due infection of the soil and of the plant is an essential to success. The evidence at the same time points to the conclusion that the soil may be duly infected for the growth of one description or some descriptions of plant, but not for some other descriptions. The field experiments on leguminous crops at Rothamsted have further shown, so to speak, that land which is quite exhausted, so far as the growth of one leguminous crop is concerned, may still grow very luxuriant crops of another description of the same family, but of different habits of growth, and especially of different character and range of roots. This result, though undoubtedly more or less due to other causes also, is, nevertheless, in some cases doubtless dependent on the existence, the distribution, and the condition, of the appropriate microbes for the due infection of the different descriptions of plant. In fact, it is pretty certain that success in any system involving a more extended growth of leguminous crops in our rotations will not be obtained without having recourse to a considerable variation in the description of leguminous plant grown. Other essential conditions of success will generally be the liberal application of potash and phosphatic manures, and sometimes chalking or liming, for the leguminous crop. Then, the questions would arise—how long the leguminous crop should occupy the land; to what extent it should be consumed on the land, or the manure from its consumption be returned; or, under what conditions the whole, or part, of it should be ploughed in? Lastly, it is probable that more benefit would accrue to the lighter and poorer than to the heavier or richer soils by any such extended growth of leguminous crop." N. H. M.

Assimilation of Free Nitrogen by Plants in its Dependence on Species, on Nutrition, and on Soil. By B. Frank (*Landw. Jahrb.*, **21**, 1—44).—1. *Dependence on Species.* (*a.*) *Cryptogams.*—Earlier investigators ascribed to the non-chlorophyllous cryptogams the power of assimilating free nitrogen (Jodin, *Compt. rend.*, **55**, 612; Hallier, *Gährungserscheinungen*, Leipzig, 1867), whilst more recently this has been denied (Nägeli, *Sitzungsber. kgl. bair. Akad.*, 1879). The author's experiments with a form of penicillium, with pure cultivations of the fungus of leguminous root-nodules, and with chlorophyllous algæ, show that, when grown in non-nitrogenous media and in air free from combined nitrogen, they will develop, although only slowly, and take up elementary nitrogen. (*b.*) *Phanerogams.*—The experiments with phanerogams were, like those previously de-

scribed (Abstr, 1891, 353), made in glass pots or in glass dishes and exposed to air. The first experiments were made with buckwheat and spurrey in sandy soil (12 kilos.); a fallow experiment with heavy loam was also made. The following results were obtained (compare results with oats and rape in loam and with yellow lupins in sandy soil, *loc. cit.*):—

TABLE I.

Kind and number of plant.	Dry produce.	Nitrogen.				
		At commencement.		At conclusion.		
		Seeds.	Sand.	Produce.	Soil.	Gain.
	grams	gram	grams	gram	grams	grams
1. Buckwheat (18) ..	10·354	0·007	1·15	0·082	(2·14)*	(1·065)
2. Corn spurrey	16·755	0·012	1·15	0·111	1·21	0·159

* Assuming the percentage given (1·0178) to be a misprint for 0·0178.

The gain in the soil was greatest in the case of yellow lupins (*loc. cit.*), and is there much too great to be due to the small amount of roots left in. In no case was there any material loss in the soil, showing that the nitrogen of the plants was derived from the air.

2. *Influence of Nutrition.*—In order to ascertain the effect of different nitrogenous manures on the amount of nitrogen fixed, experiments were made with yellow lupins which were grown in ignited sand supplied with minerals: some pots had no nitrogen, others had 0·12 gram of nitrogen, either as calcium nitrate, as ammonium sulphate, or as urea. In each case there were two sets of experiments, one microbe-seeded and the other not. There were four pots (one plant in each) for each experiment. In most cases, there were no nodules formed in those pots which were not intentionally infected, and there were generally nodules on the roots of the plants to which soil was added for seeding. The total produce, &c., was determined in each experiment (the plants of the several pots of one set being taken together). As there were some failures, the average amount of produce for the successful pots and the amount of nitrogen in it and in the seed sown is given in Table II, p. 372. The actual gain, if any, cannot be ascertained, as, with the exception of the experiments with nitrates, the final amount of nitrogen in the sand was not determined.

The results show that yellow lupins and peas, without the help of soil, develop organisms when supplied with nitrogenous manure, but there is better development when the plants are infected and are not supplied with combined nitrogen than when the plants are not infected but are supplied with combined nitrogen. In the case of yellow lupins growing in symbiosis with soil organisms, the application of nitrogenous manures (at least, as nitrate, ammonia, and urea) seems to act injuriously. Peas grow best under the simultaneous action of the symbiosis and nitrate.

TABLE II.

	Dry produce (grams).	Nitrogen.				
		At commencement.		At conclusion.		
		Seed (gram).	Nitrate, &c. (gram).	Produce (gram).	As nitrate (gram).	In produce. N in seed = 1.
Yellow Lupins.						
1. Seeded	7·859	0·009	—	0·112	—	12·3
2. Seeded + calcium nitrate	6·869	0·009	0·12	0·094	0·002	10·3
3. Not seeded + calcium nitrate	5·826	0·009	0·12	0·078	0·007	8·6
4. Seeded + am. mon. sulph.	4·890	0·009	0·12	0·051	—	5·5
5. Not seeded + am. mon. sulph.	7·088	0·009	0·12	0·049	—	5·4
6. Seeded + urea	5·598	0·009	0·12	0·092	—	10·1
7. Not seeded + urea	10·071	0·009	0·12	0·111	—	12·3
Peas.						
8. Seeded	2·264	0·009	—	0 039	—	4·2
9. Seeded + calcium nitrate	6·480	0·009	0·12	0·057	0·0015	13·4
10. Not seeded + calcium nitrate	4·350	0·009	0·12	0·052	0·0010	5·5
11. Seeded + ammon. sulph.	4·971	0·009	0·12	0·071	—	7·5
12. Not seeded + ammon. sulph.	5·468	0·009	0·12	0·048	—	5·1

3. *Influence of Soil.*—With regard to non-leguminous plants, a great difference in development was observed when oats and rape were grown in loamy soil (with 0·118 per cent. of nitrogen) and in sandy soil (containing 0·0035 per cent. of nitrogen). The results with loam have already been given (*loc. cit.*). The results given in Table III were obtained with the sandy soil.

TABLE III.

	Dry produce (grams).	Nitrogen (grams).					
		At commencement.			At conclusion.		
		Soil.	Seed.	Total.	Soil.	Produce.	Total.
1. Fallow	—	0·30	—	0·30	0·40	—	0·40
2. Oats	8·26	0 30	0·014	0·314	0·39	0·037	0·427
3. Rape	2·13	0·27	0·003	0·273	0·37	0·022	0·392

The next experiments were made with yellow lupins and with peas grown in humous soil and in peaty soil, and the results are compared with those previously obtained with the same plants grown in sandy soil (*loc. cit.*). With regard to lupins, the plants grown in sterilised, rich soil (No. 2, in Table IV) were entirely free from nodules, and lupins can, therefore, in a good soil, assimilate free nitrogen without the help of the symbiosis; the power of assimilating free nitrogen is less in good soils than in poor, light soils, but in the poor soils this action is almost entirely due to the co-operation of the fungus.

Peas can also do without the symbiosis in good soil—the plants grown in sterilised soil (No. 5) were quite free from nodules—and take up free nitrogen from the air which is collected in the crop itself and in the crop-residue in the soil. But the symbiosis is of use even in humous soil, and increases the nitrogen assimilation. Peas did not grow very well in the peaty soil; although there were nodules on the roots of plants grown in both the infected and the non-infected pots, the growth in the pot which was infected (with lupin soil) was much the greater.

The next experiments were with red clover in sand (with minerals) in humous soil, and in peaty soil. The numerical results, together with those obtained with lupins and peas, are given in Table IV (p. 374).

In the case of the sterilised red clover plants, several of the better plants grown in sand and many of those grown in soil had nodules when taken up. The results indicate that red clover, grown in sand, can only develop and take up free nitrogen when in symbiosis with the nodule fungus; otherwise, practically no nitrogen will be assimilated. In humous soil, red clover assimilates free nitrogen very readily, and enriches the soil in which it grows; the symbiosis plays an important part in the assimilation. At the same time, in spite of the symbiosis and of the presence of the necessary minerals, the growth of red clover is, in sand, far less than in a good soil. In fact, in good soil, completely or nearly sterilised, the growth is greater than in suitably infected sand. The experiments with peaty soil showed a much greater development with clover than with peas.

Summary.—All plants assimilate free nitrogen, but some of them require nitrogenous manures. There is only one plant (yellow lupin) which assimilates more nitrogen when grown in nitrogen-free soil than in presence of combined nitrogen. Peas, and probably most *Leguminosæ*, yield large amounts of nitrogen only when supplied with combined nitrogen (especially nitrates), but the amount required is less than is generally supposed. Lupins should only be grown in poor soils; peas, red clover, and probably many other *Leguminosæ* give better results when grown in good soils; the more these plants are strengthened by the application of combined nitrogen, the more free nitrogen they will be able to assimilate. Non-leguminous plants can only be made to recover from the state of hunger when grown in nitrogen-free soil by the application of combined nitrogen; when they have thus gained strength, they assimilate free nitrogen. Leguminous plants, on the other hand, recover from this period of nitrogen hunger, not only when they are supplied with combined nitrogen,

TABLE IV.

Dry produce, grams.	Nitrogen.						
	At commencement.			At conclusion.			
	Soil, grams.	Seed.	Total.	Soil, grams.	Produce.	Total.	Gain.
Yellow Lupins in Humous Soil (8 *kilos.*).							
1.* 23·326	8·6080	0·0364	8·6640	9·6640	0·2816	9·9450	1·2810
2.† 26·636	8·6080	0·0364	8·6640	7·8560	0·3475	8·2035	−0·4605
3.‡ 31·868	8·6080	0·0364	8·6640	8·7040	0·4565	9·1605	0·4965
Peas in Humous Soil (4·08 *kilos.*).							
4.* 37·983	4·3901	0·0282	4·4183	5·1122	0·7467	5·8589	1·4406
5.† 27·061	4·3901	0·0282	4·4183	5·3693	0·3705	5·7398	1·3215
6.‡ 36·682	4·3901	0·0325	4·4226	4·8307	0·6439	5·4746	1·0520
Red Clover in Sand (12·08 *kilos.*).							
7.* 44·330	0·8818	0·0457	0·9275	1·2684	0·7078	1·9762	1·0487
8† 7·184	0·8818	0·0457	0·9275	0·9543	0·0687	1·0230	0·0955
Red Clover in Humous Soil (11 *kilos.*).							
9.* 222·02	11·8360	0·0457	11·8837	11·0240	4·6406	15·6646	3·7809
10.† 165·80	11·8360	0·0457	11·8837	12·2100	2·1150	14·3250	2·4413

* Not sterilised. † Sterilised. ‡ Sterilised and seeded with humous soil.

but also when they are infected with the leguminous nodule fungus.

N. H. M.

Nitrogen Question. By H. IMMENDORFF (*Landw. Jahrb.*, **21**, 281—339).—With regard to losses of nitrogen, there is no reason to suppose that when nitrogen compounds free from nitrites and nitrates decompose without access of oxygen, free nitrogen will be liberated. This view is supported by the experimental results of Kellner (*Zeit. physiol. Chem.*, **12**, 95), Tacke (*Landw. Jahrb.*, **16**, 917), and Ehrenberg (Abstr., 1887, 172 and 746), and more recently of Schloesing (Abstr., 1890, 282). The case is, however, different when nitrites and nitrates are present in the decomposing matter; reduction takes place, free nitrogen is liberated, and all the intermediate oxy-

compounds will be formed (Tacke, *loc. cit.*). In Tacke's experiments, the reduction was diminished, but not altogether prevented, by the presence of air, and it is possible that with still better ventilation the reduction might have been stopped altogether. Losses of nitrogen during the process of nitrification was observed by Dehérain (Abstr., 1887, 993), and Tacke (*Landw. Jahrb.*, **18**, 439), whilst in Ehrenberg's experiments (*loc. cit.*), in which, however, ventilation was deficient, no evolution of free nitrogen was detected, and Schloesing's results (Abstr., 1889, 638 and 1239) indicated that a loss of free nitrogen is not necessarily a consequence of nitrification.

The power of fixing nitrogen, which Berthelot ascribes to some especially poor soils, was in no case confirmed by Schloesing (Abstr., 1888, 1330); not even after two years exposure of a soil to air. On the other hand, Berthelot's results are supported by those of Gautier and Drouin, Dehérain, Pechard and Tacke (*loc. cit.*). Inasmuch as no constituent of soils is known to have the power of fixing nitrogen, the fixation, if admitted at all, is ascribed to bacteria; and it seems not unlikely that the soil bacteria which fix nitrogen are identical with those which, as has been shown by the indirect experiments of Hellriegel and others, and the direct experiments of Schloesing and Laurent, have the same power when living in symbiosis with leguminous plants. It may be mentioned, however, that in Berthelot's experiments, sterilised soils and soils infected with the contents of leguminous nodules, showed no material difference with regard to the amount of nitrogen they fixed.

In the first series of the author's experiments, mixtures of blood meal, garden soil, and chalk, and of bone meal, soil, and chalk respectively were kept for some months, at a temperature of 28—30° in glass tubes, from which all the air had been expelled and replaced by oxyhydrogen mixture (prepared by electrolysis). The different parts of the apparatus, of which a sketch is given, were fused together, so as to avoid the use of joints or corks; and it was so arranged that samples of the gas could be obtained as often as desired for analysis, without interrupting the experiment. In the first weeks, no appreciable amount of nitrogen was evolved, but subsequently there was a loss in Experiment 1 (with 14·856 grams of substance, containing 0·3151 gram of nitrogen) of 20 miligrams of nitrogen. In Experiment 2 (with 14·3969 grams of soil, &c., containing 0·2208 gram of nitrogen) the loss of nitrogen was 11 milligrams. No nitrous oxide was given off.

In the other series of experiments, layers of soil or other substances were put in alternate layers with pieces of glass rod in upright cylinders, so constructed that air free from combined nitrogen could be passed through from below, and any ammonia which might be given off absorbed by acid, and the quantity determined at the end of the experiment.

The following table shows the nature and amounts of the substances experimented on, the total initial and final nitrogen; the nitrogen as nitric acid, and the nitrogen as ammonia, found at the end of the experiments. The experiments 1—6 extended over nearly a year, whilst the others lasted from 16 to 22 weeks.

	Nitrogen.					
	At commencement.	At conclusion.				
				As ammonia.		Gain or loss.
	Total.	Total.	As nitrate.	In soil.	In receiver.	
	grams	grams	gram	grams	gram	gram
1. Arable soil (100 grams)..	0·1198	0·1078	0·0311	—	0·0008	−0·0120
2. „ „ ..	0·1214	0·1144	0·0196	—	0·0006	−0·0070
3. Arable soil (100 grams), sterilised	0·1209	0·1252	0	—	0·0033	+0·0043
4. Lupin soil (100 grams) ..	0·1061	0·0830	0	—	0·0006	−0·0231
5. „ „ ..	0·1045	0·0852	0	—	0 0006	−0·0193
6. Lupin soil (100 grams), sterilised.....	0·1042	0·1044	0	—	0·0056	+0·0002
7. Arable soil (100 grams), and ammonium sulphate containing 0·115 gram of nitrogen.....	0·2363	0·1876	0·0362	0·059(	trace	−0·0487
8. Arable soil (100 grams), with bone meal (5 grams)	0·3169	0·2973	0·1092	trace	trace	−0·0196
9. Lupin soil (100 grams), with bone meal (5 grams)	0·2890	0·2821	0·0454	0·0979	0·0678	−0·0069
10. Bone meal (9·4775 grams), chalk (2 grams)	0·4484	0·4655	0	0·2816	0·1500	+0·0171
11. Bone meal (9·9702 grams)	0·4717	0·4851	0	0·3073	0·0671	+0·0133
12. Blood meal (10·4945 grams), chalk (2 grams).	1·4074	1·4284	0	1·0781	0·8149	+0·0210
13. Horn meal and superphosphate* (equal parts; 21·034 grams)	0·3660	0·3620	0·0132	0·1978	0	−0·0040
14. Horn meal and superphosphate† (21·002 grams)..	0·4250	0·4180	0·0033	0·1997	0·0020	−0·0070
15. Horn meal and superphosphate-gypsum (22·9694 grams)	0·4154	0·4190	0·0049	0·1578	0·1018	+0·0036
16. Bone meal (10·8041 grams), and gypsum (12 grams)	0·4500	0·4284	0	0·2620	0·1170	−0·0216
17. Bone meal (12·1033 grams), and kainite (8 grams)	0·4987	0·4676	0	0 2434	0·0555	−0·0310
18. Bone meal (10·6834 grams), and chalk (10 grams)	0·4402	0·4317	0	0·2743	0·2578	−0·0087

* Containing 33·7 per cent. of soluble phosphoric acid.
† Containing 8·6 per cent. of soluble phosphoric acid.

With regard to loss of free nitrogen, the results show that it may take place during decomposition in presence of plenty of oxygen, both when nitrification takes place and when ammonia is formed. Gain of nitrogen took place (Experiments 10, 11, 12) in substances containing plenty of nitrogen, and coincidently with large production of ammonia. As other experiments indicate that under these conditions loss of free nitrogen takes place, this was probably also the case in these three experiments, and the gain must therefore have been still greater than the numbers indicate. The last six experiments are of further interest as showing the retentive power, or want of such a power, for ammonia of various substances. The superphosphate retained the whole of the ammonia; the superphosphate-gypsum, and gypsum kept back some, but allowed very much to escape. Kainite, on account of its greater solubility, acts more strongly in fixing ammonia than either superphosphate-gypsum or gypsum. Calcium carbonate assists the volatilisation of ammonia. When phosphoric acid was used, there was no loss of free nitrogen, whilst when other substances, especially kainite, were employed, the loss of free nitrogen was considerable. The author is, however, not prepared to say that the non-evolution of nitrogen was due to the presence of phosphoric acid (compare v. Krause, Abstr., 1890, 1340).

In the course of the first series of experiments, it was noticed that when the tube containing soil was filled with electrolytic gas, the gas disappeared entirely in a few days. In order to ascertain whether this was due to the physical and chemical properties of the soil, or to micro-organisms, the following experiments were made:—25 grams of moderately moist arable soil was put into the apparatus (similar to that used in the first set of experiments already described), which was exhausted and filled with the oxyhydrogen mixture. In the first four weeks there was only a slight absorption, but a good deal of carbonic anhydride was evolved; afterwards the absorption was more rapid, and in about five weeks almost the whole of the gas was absorbed, and nearly a vacuum produced. A similar experiment in which a few drops of chloroform were introduced into the apparatus showed that under these conditions only a trace of carbonic anhydride was given off, and that no absorption of the oxyhydrogen mixture took place. Two more experiments were made in which blood meal (5 grams) was mixed with the soil; similar results were obtained. The absorption of oxygen and hydrogen is therefore probably due to micro-organisms in the soil. The author considers this power of uniting oxygen and hydrogen to be more remarkable than the power of fixing nitrogen, and refers to the processes studied by Winogradsky, in which bacteria oxidise ferrous oxide to ferric oxide, hydrogen sulphide to sulphur, and finally to sulphuric acid, &c.

Experiments were also made to see if pure cultivations of bacteria from pea and bean nodules have the power of assimilating free nitrogen, but they always failed to develop well in nutritive solutions free from nitrogen.

The following conclusions are drawn from the above results:—(1.) Loss of nitrogen can take place in decomposing nitrogenous

matter, independently of nitrification; whilst it does not take place when air is excluded. (2.) It is not established whether free nitrogen is eliminated during the nitrification of ammonia with sufficient ventilation. (3.) Free nitrogen is fixed not only in poor soils, but in materials rich in nitrogen. (4.) Superphosphates are excellent preservatives for farmyard manure, even when air has access. Superphosphate-gypsum is of less value, whilst gypsum and kainite are far less effective still. (5.) Arable soil, after undergoing a process of decomposition, has the power of uniting oxygen with hydrogen, the union being probably accomplished by bacteria. (6.) No kind of bacteria has as yet, with certainty, been isolated which has the power of fixing free nitrogen; although it is established that the *Leguminosæ*, with the help of certain known bacteria, are in a position to employ free nitrogen to their advantage.

Sketches are given of the apparatus employed, which was similar to that used by Tacke.

After the above investigation was completed, the author found that the absorption of oxygen and hydrogen by soils had been discovered by de Saussure, in 1834. Liebig (*Annalen*, **153**, 142) considered the process to be a purely chemical one. N. H. M.

Fixation of Free Nitrogen by Plants. By T. Schloesing, Jun., and E. Laurent (*Compt. rend.*, **113**, 776—778).—An extension of the work on the Leguminosæ (Abstr., 1891, 353) to other classes of plants. Two experimental methods were employed, the first consisting in measuring the decrease in volume of the nitrogen of the atmosphere in which the plants were confined, the other in estimating the increase of the total nitrogen in the soil, seeds, and crop during the experiment. The results yielded by the two methods agree well. As the conditions under which nitrogen might be absorbed were unknown, it was necessary to employ natural soil, for which purpose a poor sandy earth was enriched with calcareous earth, and with garden soils in which grass, trefoil, lupin, and beans had been grown; it was watered with nutritive mineral solutions also, and, after the seeds had been sown, with an aqueous extract of the mixture of garden soils.

In the first set of experiments, which extended over $3\frac{1}{2}$ months, the results were obscured by the growth of mosses and algæ on the surface of the soil, and although it was found that the nitrogen absorbed was markedly greater in the case of the leguminous plants (peas) than in those of the others (Jerusalem artichokes, oats, and tobacco plants), yet it could not be ascertained to which vegetation the absorption was due. That nitrogen was assimilated during the growth of the cryptogams was evident, since in one of the blank experiments in which no appreciable growth appeared on the surface of the soil, no sensible amount of absorption took place, whilst in other blank experiments in which the lower growths had developed freely, a considerable amount of nitrogen was taken up.

In a second set of experiments, which extended over three months, the lower growth was prevented by covering the soil with a layer of calcined quartz sand, and it was found that neither with soil alone,

nor with growing plants of oats, mustard, cress, or asparagus, was there any sensible absorption, whilst with peas, a very considerable amount of nitrogen was found. In the last case it was remarked, too, that nodosities had formed on the roots.

Berthelot (*ibid.*, 778—779), in calling attention to the above note, points out the confirmation which the results bring to his own researches and views on this subject. Jn. W.

Proteïds of the Maize-kernel. By R. H. Chittenden and T. B. Osborne (*Amer. Chem. J.*, **13**, 453—468; compare Abstr., 1891, 1285). —The authors propose to investigate, first, the proteïds which are soluble in salt solution, but insoluble in water; secondly, those which are soluble both in water and in salt solution, and, thirdly, those which are insoluble in water and salt solutions, but soluble in alcohol. The present paper relates to the first class.

When fine freshly-ground maize-meal is extracted in the cold with 10 per cent. sodium chloride solution, it yields a yellow solution, from which the proteïds may be precipitated either by removing the salt by dialysis or by adding ammonium sulphate to saturation. The precipitate is purified by redissolving in sodium chloride solution and again dialysing, and then separates in small spheroïds, which adhere to the walls of the dialyser, and closely approximate to crystals in character. The ammonium sulphate precipitate is partially soluble in water, and may therefore be treated with that solvent before digesting with sodium chloride, the two solutions being mixed before dialysing. 5 per cent. ammonium chloride solution may be substituted for the sodium chloride, the proteïds being precipitated as before by ammonium sulphate. The products obtained in this way were of practically identical composition:—C, 51·65; H, 6·82; N, 17·69; and S, 0·93. The yield of pure product obtained by the first method was 0·2 per cent.

When the sodium chloride solutions of the proteïds are heated, they become turbid, and at a somewhat higher temperature form a flaky coagulum; if this is filtered off, the clear filtrate undergoes the same changes when raised to a still higher temperature, and so on, several distinct fractions being obtained; even when the solution has been boiled for some time, the filtrate often yields a precipitate with acetic acid. The temperatures of coagulation are not, however, very constant, as they are considerably altered by slight variations in the methods of extracting and purifying the proteïds. From a consideration of these phenomena it appears that the proteïd matter either consists of several distinct globulins, or is itself a simple globulin capable of being split up by the action of heat. It may, for instance, be a mixture of variable proportions of vitellin and an uncoagulable globulin. Phytomyosin cannot be present in quantity since very little precipitate is thrown down when the sodium chloride solution of the proteïd is saturated with that salt.

An attempt was made to fractionate the proteïd matter based on the facts that it is not entirely redissolved by sodium chloride solution, and that the soluble portion is only partially reprecipitated by the addition of a large quantity of water. The fractions soluble in

sodium chloride were of practically the same composition as the original proteïds, but the insoluble fraction contained appreciably less nitrogen (15·59 per cent.). The formation of the insoluble proteïd may be explained by supposing that the globulin is partially converted into an albuminate. Another attempt was based on the varying solubility of the proteïd in sodium chloride solutions of different strengths; but the fractions obtained were unaltered in composition. Jn. W.

Choline and Betaïne in Cotton Seed Foods. By W. Maxwell (*Amer. Chem. J.*, **13**, 469—471).—The bases were extracted from finely ground cotton-seed cake with 70 per cent. alcohol, and purified by means of the mercurochlorides. The hydrochlorides prepared from the latter were separated by means of absolute alcohol, in which the betaïne salt is very sparingly soluble. The relative amounts of choline and betaïne hydrochloride thus obtained were as 1 to 5·7. The relative amounts obtained from cattle food prepared from a sample of the same cotton seed was as 1 to 4·7. Jn. W.

Occurrence of Gums which yield Xylose. By A. Voswinkel (*Chem. Centr.*, 1891, ii, 655; from *Pharm. Centralhalle*, **32**, 505—507).—The author found these gums in several fungi, *Cantharellus cibarius*, *Hydnum repandum*, *Clavaria flava*, *C. botrytis*, *Psaliota campestris*, *Boletus edulis*, and *B. granulatus*. It was separated by extracting the ground fungus with soda; the extract was then precipitated with alcohol, and the precipitate washed with alcohol containing a little hydrochloric acid. The product gave the phloroglucinol and furfuraldehyde reactions, and was converted into xylose by dilute sulphuric acid. J. W. L.

The Poisonous Constituent of the Ethereal Fern Extract. By E. Poulson (*Chem. Centr.*, 1891, ii, 673; from *Arch. expt. Path. Pharm.*, **29**, 1—24).—The author's experiments show that the poisonous properties of fern extract are due to an amorphous substance which is the true *filicic acid*. The acid is readily converted into its lactone, by simply boiling its ethereal solution. The lactone is named *filicin* by the author. The filicic acid melts at 184·5°; filicin melts at 125°. The pure acid may be obtained from filicin by dissolving the latter in cold dilute soda, and filtering the solution into dilute hydrochloric acid. The white precipitate is then dried over sulphuric acid. Determinations of the molecular weights of the two compounds by Raoult's method gave for filicin 642 and 654, which, in conjunction with the analysis, indicates the formula $C_{35}H_{40}O_{12}$, whilst, for filicic acid, the numbers 663—699 were obtained, and this, in conjunction with the analysis, indicates the formula $C_{35}H_{42}O_{13}$. The author considers filicic acid to be suitable for therapeutical purposes; it is readily soluble in the alimentary canal, but difficultly reduced and either kills parasitic organisms or expels them, without damaging the canal. It appears to be more readily absorbed if taken with oil than if taken alone. J. W. L.

Ammonia in the Atmosphere and Rain Water of the Tropics. By V. Marcano and A. Muntz (*Compt. rend.*, **113**, 779—781).—The observations, which extend over several years, were made near Caracas, Venezuela, in 10° N. latitude, at an altitude of 922 metres above sea-level. The temperature of this locality is constant, the rains very intermittent, and the storms violent and numerous. It has already been shown (Abstr., 1889, 923) that the nitric and nitrous nitrogen in the air of this region is ten times more abundant than in that of more temperate climates, and it is now found that the ammonia is distinctly less, a surface of acidified water 1 square metre in area absorbing in 24 hours an average of 0·01252 gram of ammonia, as against 0·02 and 0·024 in France. This unexpected result is probably due to the formation of solid ammonium nitrite and nitrate in the air, a theory borne out by the excessive amount of ammonia found in the rain water, 0·00155 gram per litre on an average, as against 0·00052 gram in Alsace (Boussingault) and 0·00097 at Rothamsted (Lawes and Gilbert). (Compare, however, next abstract.) Jn. W.

Ammonia in Rain Water. By Albert-Lévy (*Compt. rend.*, **113**, 804—805).—The author points out that the figures of Lawes and Gilbert quoted by Marcano and Muntz (preceding abstract) varied considerably from year to year, and that, in 1856 for example, they found 0·00143 gram of ammonia per litre, an amount quite comparable with those obtained by the authors criticised. He also quotes various other data to show that the amount of ammonia in the rain water of Venezuela is not excessive; the mean amount, for instance, in the rain water of Montsouris, France, where he has estimated the ammonia in every downpour for upwards of 16 years, is as much as 0·0022 gram per litre. Jn. W.

Analytical Chemistry.

Test for Hydrogen Peroxide. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 22—23; compare Abstr., 1891, 1549).—The author claims priority over Denigés for the use of the ammonium molybdate and sulphuric acid test for hydrogen peroxide (Abstr., 1890, 1185). He further states that the test is not trustworthy, as it is coloured yellow by faint traces of organic matter and by hydrogen phosphate and silicate, and yields a blue coloration when the test is made on alcoholic or aldehydic derivatives. The following test is without these disadvantages:—To the suspected liquid, 3 or 4 c.c. of ammonium molybdate solution (10 per cent.) is added, and subsequently a few drops of citric acid solution (25 per cent.); if hydrogen peroxide be present, a yellow coloration ensues. This test is capable of detecting 1/10 milligram hydrogen peroxide in 400 c.c. water. The author notes that commercial paraldehyde contains notable quantities of hydrogen peroxide. T. G. N.

Standardising Iodine Solution for the Determination of Sulphur in Steel and Pig Iron. By J. M. Wilson (*Chem. News*, **64**, 252).—Using a standard steel, the author standardises his iodine solution by the same process as he uses for the determination of sulphur in the samples of pig-iron and steel submitted for analysis, and finds the result satisfactory. D. A. L.

Estimation of Sulphur. By G. Craig (*Chem. News*, **64**, 266—267).—20 grains of slag, finely ground, is heated with 1 oz. of water, in a flask furnished with a tap funnel, with a nitrogen bulb partially filled with glass beads and charged with ammonia and hydrogen peroxide for outlet, and with a Liebig's bulb charged with potash and hydrogen peroxide for inlet through which coal gas is now admitted to expel air; the heating is continued, and hydrochloric acid is run in from the funnel, the whole is agitated until the slag is decomposed, boiled, and finally coal gas is aspirated through. The nitrogen bulb is now washed out, and the sulphur determined as barium sulphate. To make the estimation in pyrites, the finely pulverised ore, well mixed with zinc-dust in a small Bohemian glass tube, is covered lightly with the disc-like end of a flattened glass rod, which is packed round with asbestos, the tube is heated at first gently, finally for 30 seconds at a red heat; it is then, when cool, dropped into a flask like that employed above, but fitted at the outlet with a reflux condenser, a U-tube containing calcium chloride, and finally, a U-tube filled with glass beads and sodium hydroxide. The operation proceeds as described above, but the hydrogen sulphide is not oxidised. D. A. L.

Estimation of Sulphur in Organic Substances. By A. Angeli (*Gazzetta*, **21**, ii, 163—165).—Some organic substances containing sulphur resist the oxidising action of nitric acid when heated with it in a sealed tube for determination of the sulphur by Carius' method. The author finds that the addition of bromine very considerably assists the oxidation; for example, sulphonal, which offers great resistance to oxidation by nitric acid alone, is completely oxidised when heated with nitric acid of sp. gr. 1·52 and bromine for six hours at 210°. W. J. P.

Estimation of Phosphoric Acid in Slags. By V. Edwards (*Chem. News*, **64**, 275).—A slag which resisted aqua regia succumbed satisfactorily to the action of boiling concentrated sulphuric acid in the presence of some mercury; the resulting liquid, when cold, was diluted, and an aliquot part filtered, and precipitated directly with citro-magnesic solution and ammonia. The precipitate was dissolved in nitric acid and titrated with uranium solution. D. A. L.

Estimation of Arsenic in Wall-paper. By C. R. Sanger (*Amer. Chem. J.*, **13**, 431—453)—To avoid the waste of time, the inconvenience of using large quantities of material, and the introduction of large percentage errors in weighing which are involved in the ordinary form of the Marsh process, it is modified in order that the

mirror obtained under standard conditions may be compared with a set of standard mirrors obtained under the same conditions from known amounts of arsenious anhydride.

20, 50, or 100 sq. cm. of the paper, according to the size of the pattern and the amount of arsenic present, as judged by the colour of the paper and its smell when burned, is cut into small pieces and charred by heating with 1—5 c.c. of strong nitrosulphuric acid (1 : 30), the excess of nitric acid being afterwards expelled. The use of an oxidising agent is essential, owing to the presence of chlorides, which would cause the volatilisation of 12—60 per cent. of the arsenic, and of sulphur compounds such as ultramarine, which would cause its retention as insoluble sulphide. Nitric acid is recommended, as it is simple and speedy in action; the oxidation of the arsenic is immaterial, as arsenic salts are found to yield the same results as arsenious salts; and the presence of small quantities of nitric acid in the Marsh flask does not cause the retention of the arsenic, as stated by Blondlot (*Compt. rend.*, **57**, 596).

The charred mass is moistened, and then thoroughly broken up with 5 c.c. of water; the sulphurous anhydride is expelled by boiling, as otherwise arsenious sulphide may be formed during the subsequent operations, the liquid is filtered into a tared test-tube, and the residue is repeatedly washed with hot water. If a filter-pump is used, the filtrate and washings need not amount to more than 35 c.c. The extract is now ready for reduction in the modified Marsh apparatus.

This consists of a wide-mouthed, india-rubber-stoppered bottle of 75 c.c. capacity, provided with a funnel-tube for introducing liquids, and connected on the one hand with a continuous hydrogen apparatus, and on the other with a tube of fused calcium chloride leading to a hard glass reduction-tube. Sulphuric acid cannot be used as a desiccating agent, as it dissolves the hydrogen arsenide. The reduction-tube, of 7 mm. bore, is drawn out at the end to 1·5—2·0 mm. bore, and bent up and sealed. At the commencement of each operation, the bottle is charged with 3 grams of finely-granulated zinc, and, the tightness of the apparatus having been tested, the end of the reduction-tube is broken, 20 c.c. of dilute (1 : 8) sulphuric acid is run into the flask, and hydrogen is turned on from the generator, and burned at the end of the reduction-tube in a flame 1—2 mm. high. By the use of an additional hydrogen generator the necessity for stimulating the evolution of hydrogen in the Marsh flask is obviated; it may be necessary even to cool the liquid. The use of hydrochloric acid in either the generator or the flask is inadmissible, as the mirror is then liable to be contaminated with zinc chloride. The air having been thoroughly expelled, the constricted part of the reduction tube is heated by a Bunsen flame kept steady by an iron cone. No mirror should appear in the course of 20 minutes.

The prepared extract is now gradually introduced through the funnel-tube, the lower end of which is constricted to avoid the mechanical introduction of air. The amount added, which should not contain more than 0·06 milligram of arsenious anhydride, is determined by weighing the test-tube before and after. After 25 minutes, the whole of the arsenic has been transferred to the

reduction-tube, as if the action is continued until all the zinc has dissolved there is no increase in the density of the mirror.

The mirror is now compared with a standard set, made in a similar way from quantities of arsenious anhydride varying from 0·005 to 0·06 milligram. These standards, which must be kept in the dark to avoid oxidation, are best mounted in frames which, together with a frame containing the specimen under examination, can be mounted horizontally in a box resembling a stereoscopic camera, so that the comparison may be made by transmitted light. As small an amount as 0·001 milligram of arsenious anhydride can be detected by the process.

As a check on the results obtained, the arsenic in the various samples of paper examined was estimated by titration with iodine, after solution and reduction with sulphurous anhydride. The organic matter was separated by igniting the paper with potassium nitrate, by charring it with nitrosulphuric acid, or by distilling it with hydrochloric acid. The results agree well. Jn. W.

Estimation of Boric Acid. By O. Hehner (*Analyst*, 1891, 141—145).—Stolba long ago proposed to fix boric acid in solution by adding a known excess of borax and igniting the residue. The author finds that very good results may be obtained, but that the greatest caution is necessary to avoid loss by spirting during the ignition of the residue.

After unsuccessfully attempting to fix the boric acid by means of ammonia or sodium carbonate, the author has succeeded in getting excellent results by the addition of a known weight of sodium pyrophosphate in the shape of disodium hydrogen phosphate.

L. de K.

Estimation of Combined Alkali in Soap. By J. A. Wilson (*Chem. News*, **64**, 205).—The total alkali having been determined in the usual manner, the alkali as soap is ascertained in the following way:—A weighed quantity of soap is decomposed, on a water-bath, with dilute sulphuric acid, cooled in ice, filtered, and the fatty acids washed three times successively with 250 c.c. of boiling water, cooling and filtering each time. Then, to determine the proportion of the alkali of the soap in combination with the soluble fatty acids, the united filtrates are made up to 1 litre and 500 c.c. of the solution titrated with decinormal alkali, using methyl orange as indicator in the first instance, and finishing off with phenolphthaleïn; the latter numbers, calculated to caprylic acid, are those required. The insoluble fatty acids are dried, weighed, dissolved in alcohol, and the alkali originally combined with them estimated by titrating with semi-normal alkali.

Or the acid, equivalent to the alkali existing in all forms, is obtained by decomposing the soap with standard sulphuric acid, titrating the excess with methyl orange and deducting it from the total quantity of acid employed. D. A. L.

Separation of Manganese and Zinc. By E. Donath (*Ber.*, **24**, 3600—3602).—A question of priority.

Estimation of Manganese in Slags and Ores. By G. L. Norris (*Chem. News*, **64**, 242—243).—A gram of finely powdered slag, moistened with water, is mixed with 50 c.c. of nitric acid (sp. gr. 1·420), heated to boiling, treated with 3 or 4 c.c. of hydrofluoric acid and boiled for a few minutes, when the decomposition is complete. More nitric acid is added, the whole heated to boiling, and the manganese precipitated with potassium chlorate. The precipitate, collected on an asbestos filter, is either finally weighed as pyrophosphate, or is dissolved in standardised ferrous sulphate or oxalic acid, and the excess of solvent titrated with potassium permanganate.

With ores, tartaric acid is added before the hydrofluoric acid, or when much iron is present in the ore these acids are added together; the excess of the latter being boiled off and of the former decomposed, and the estimation proceeded with as above. D. A. L.

Quantitative Separation of the Metals of the Hydrogen Sulphide Group by Means of Bromine Vapour. By P. Jannasch and P. Etz (*Ber.*, **24**, 3746—3748).—The quantitative separation of bismuth and cadmium may be readily effected by precipitating the metals with hydrogen sulphide, and after drying and weighing the mixed sulphides, transferring them to a porcelain boat, which is placed in a combustion tube and gently heated in a rapid stream of air and bromine vapour; the bismuth volatilises, and is condensed in an absorption apparatus containing dilute hydrochloric acid. The operation occupies about half an hour. The residual cadmium bromide may be dissolved in a small quantity of hydrochloric acid and precipitated with sodium carbonate. The bismuth solution is treated with nitric acid and evaporated to dryness, and this operation repeated until all the hydrochloric acid has been eliminated; the bismuth is then precipitated with ammonium carbonate solution containing a little ammonia.

The analytical results agree very closely with the theoretical numbers. J. B. T.

Separation of Bismuth from Lead. By W. Remmler (*Ber.*, **24**, 3554—3556).—The author has studied the method of separating bismuth from lead, based on the volatility of bismuth chloride, and finds that the two chlorides can be easily and accurately separated by heating the mixture at the boiling point of sulphur.

For this purpose he employed a small apparatus consisting of two test-tubes placed one inside the other, the space between them containing the sulphur; the mixture of the two chlorides is placed in a much smaller tube, and is introduced into the apparatus by means of a glass rod, which is bent into a ring at its lower extremity; during the heating, which lasts an hour, a stream of dry chlorine is passed into the small tube containing the substance.

When the two metals are obtained as sulphides, as is usually the case, the mixture is first heated for an hour in a xylene bath, and then for a like period in the sulphur bath, a stream of chlorine being passed during both operations; by this means the sulphides are first

converted into chlorides, and then the bismuth chloride is completely volatilised. An analysis of a mixture of the metals containing 42·17 per cent. of lead gave in this way 42·09 per cent.; another sample containing 43·74 per cent. of lead gave 43·43 per cent.

F. S. K.

Reaction of Certain Essences with Manganous Salts. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 25—29).—When turpentine is shaken with an ammoniacal manganous solution, and a current of air is passed through the mixture, the hydrocarbon becomes coloured dark brown. Although this reaction occurs with both dextro- and lævo-gyrate varieties, it does not obtain with pinene or fresh steam-distilled turpentine. Pure pinene exposed to dry or moist air for a day or two gives the reactions of hydrogen peroxide, and also reacts as an aldehyde with alkaline potassiomercuric iodide solution, with magenta in sulphurous acid, and with metamidobenzene hydrochloride, but does not give the above described reaction unless it has been kept for two to three months in half-filled vessels, when it gradually acquires the property; this is probably due to the formation of acids by partial oxidation of the pinene, since traces of fatty acids dissolved in pinene or freshly distilled thyme, lemon, or turpentine oil at once determine the reaction described. Turpentine and lemon oils which have resinified do not react, since they are deficient in pinenes, which are necessary both as solvents of the manganese salt and as sources of hydrogen peroxide. To determine the nature of the brown substance, 10 kilos. of French turpentine oil were treated with ammoniacal manganous solution, and a current of air passed through the warmed emulsion. The brownish-black essence, after distillation at a pressure of 10—15 mm., was treated with alcohol, when it formed a brownish-black mass; this, after washing with alcohol, was taken up with chloroform (in which it was freely soluble), and reprecipitated from this solvent by alcohol. As thus obtained, it forms a greyish powder which is insoluble in water, and only slightly soluble in alcohol, but freely so in carbon bisulphide, ether, and chloroform, yielding brownish-black solutions.

Analysis points to the formula $Mn_2C_{18}H_{28}O_6$, and the author considers the substance to be the manganese salt of an acid $C_9H_{14}O_2$, produced together with formic acid by oxidation of the turpentine molecule, since he finds that formic acid is a constant product of turpentine oil distillation, and turpentine solutions of the brown product deposit crystals of manganous formate. The solution of the brown substance in ether is decomposed by hydrogen chloride with formation of anhydrous manganous chloride, but evaporation of the residual ether gave no defined result. The brown substance, treated with hot sodium hydroxide solution, filtered, acidified, and extracted with ether, yielded odorous pitchy substances, which did not crystallise.

T. G. N.

Detection of Turpentine and other Impurities in Essences. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 29—30; compare preceding abstract).—Hydrogen potassium tartrate (20 grams) is neutralised with manganous carbonate (5—6 grams), and dissolved in a litre of water.

5 c.c. of the essence to be tested, 3 c.c. of the above solution, and 5 drops of ammonia solution (sp. gr. 0·925) are well shaken together in a test tube, which is then placed in a water bath, and a current of air passed through the contents for 30 seconds; the tube is then removed, its contents well shaken, and allowed to separate. With the exception of the oils of lemon and bergamot, which are coloured dark brown, the majority of pure essences are but faintly tinged with yellow, whereas the addition of turpentine determines a coloration varying from brown to intense brown-black in the supernatant essence. T. G. N.

Analysis of Spirits. By J. Bell (*Analyst*, 1891, **185**, 171—174).—*Estimation of the Free Acids.*—50 c.c. of the spirit, previously reduced to proof strength, is distilled to dryness in a glass retort. The distillate is titrated with N/10 barium hydroxide, using phenolphthaleïn as indicator. To ascertain the nature of the acid, the liquid is evaporated to dryness, and the barium salt weighed. Its combining weight is then found by converting it into sulphate.

Estimation of Ethereal Salts.—50 c.c. of the spirit at proof strength (redistilled if necessary) is directly neutralised with N/10 barium solution. The spirit is then placed in a glass retort, and distilled to dryness, the first 30 c.c. being collected separately. The distillates are now heated, in a closed flask, with a known volume of N/10 barium hydroxide, the excess of which is afterwards titrated. 1 c.c. of the barium solution corresponds with 0·0088 gram of ethyl acetate. The true nature of the compound may be ascertained by an analysis of the dry organic barium salt.

Estimation of the Higher Alcohols.—100 c.c. of the spirit at proof strength is digested with an excess of barium hydroxide, and then distilled almost to dryness. The distillate is then further diluted until it is 70 u. p., and repeatedly shaken out with chloroform. The latter, after having been repeatedly washed with water to remove any ethyl alcohol, is oxidised with a mixture of sulphuric acid and potassium permanganate, in a closed flask, at a temperature of 80° F. This operation takes about three days, and the mixture must be repeatedly shaken during that period. When the oxidation is complete, the excess of permanganate is reduced by a few drops of sulphurous acid, and the liquid rendered distinctly alkaline with normal soda. After removing any chlorine with silver sulphate, the aqueous filtrate is distilled with 10 c.c. of normal sulphuric acid, and the distillate received into a solution of N/10 barium hydroxide.

From the amount of barium neutralised, and the subsequent examination of the organic barium compound, the quantity of the higher alcohols may be calculated by employing the usual factors.

L. de K.

Estimation of Sugars by Means of Ost's Copper Solution. By M. Schmoeger (*Ber.*, **24**, 3610—3620).—A number of quantitative experiments were made in order to ascertain whether sugars can be accurately estimated with the copper solutions described by Ost (Abstr., 1891, 125, 1298), for which he claims many advantages over Fehling's solution; the experiments confirmed Ost's statements

in all respects except, perhaps, as regards the stability of the more concentrated copper solution, because, on long keeping in glass vessels, a deposit of copper silicate is formed in this solution.

Sugar, in solutions containing calcium, cannot be directly estimated by Ost's method because, on boiling, calcium carbonate is precipitated and the weight of the copper oxide is thereby increased considerably; in such cases, the calcium may be removed by precipitation with potassium oxalate, and the analysis then carried out as usual, as the presence of a small quantity of oxalic acid does not affect the results.

F. S. K.

Analysis of Sugar, Molasses, and Syrup. F. W. Babington (*Analyst*, 1891, 181—185).—*Saccharimeter Readings.*—The author dissolves 13·024 grams of the sample in 50 c.c. of warm water in a flask of 100 c.c. capacity, adds 1 gram of purified animal charcoal, and after agitating occasionally for half an hour, mixes with 30 c.c. of alumina cream. After making up to 100 c.c. and filtering through a dry filter, the liquid is examined in the 20 cm. tube in a Soleil-Ventzke-Scheibler apparatus.

Clerget Inversion.—50 c.c. of the same solution is mixed with 2·5 c.c. of fuming hydrochloric acid and heated during 20 minutes at a temperature of 60—70°. After cooling and making up to a volume of 55 c.c., the liquid is examined in the 22 cm. tube. The following formula is then applied:—

$$\frac{(\text{Direct reading} + \text{invert reading})\ 200}{142{\cdot}7 - \frac{1}{2}\ \text{temperature of inverted solution}} = \text{p. c. of cane sugar.}$$

Reducing Sugars.—The author prefers the gravimetric estimation by means of Fehling's solution. The cuprous oxide is collected on a weighed asbestos filter and weighed as such. If 2·5 grams of the sample has been used, the percentage of reducing sugars will be found by multiplying first by 0·4861 and then by 40. If it is desired to also estimate the cane sugar gravimetrically, 0·25 gram of the sample must be inverted as in Clerget's process, and then again carefully neutralised with sodium carbonate.

Moisture and Water.—The moisture in ordinary moist sugars is estimated by drying 2 grams to constant weight, but in the case of syrups or molasses, 20 grams of the sample is dissolved in water and made up to 100 c.c. 20 c.c. of this solution (= 4 grams of sample) is put into ordinary asbestos fibre contained in a milk tube, the tube and contents having been previously dried and weighed. The tube is then placed in a water-bath and dried for 48 hours at a temperature of 90—100°. The increase of the weight of the tube and contents gives the amount of dry substance contained in 4 grams of the sample, water being found by difference.

L. de K.

Estimation of Furfuraldehyde and of Pentoses. By A. Günther, G. de Chalmot, and B. Tollens (*Ber.*, **24**, 3575—3585).—After replying to some observations of Stone (this vol., p. 247), the authors describe two methods for the estimation of pentoses in vegetable products (compare Abstr., 1891, 769). In the first method, the

finely-divided substance (5 grams) is distilled from a flask with hydrochloric acid of sp. gr. 1·06 as long as the distillate gives a red coloration with aniline acetate paper, fresh hydrochloric acid being added from time to time as that in the flask passes over; this process generally occupies 4—6 hours. The distillate is neutralised with solid sodium carbonate, then acidified with acetic acid, and titrated with a solution of phenylhydrazine of known strength until a drop of the mixture no longer gives a reaction with aniline acetate paper; the quantity of furfuraldehyde in solution being thus determined, the percentage of arabinose or xylose is calculated by multiplying by factors which are obtained by ascertaining the quantity of furfuraldehyde formed from the pure pentoses under the same conditions. If, for example, 5 grams of a substance containing arabinose gives 0·75 gram or 15 per cent. of furfuraldehyde, this quantity must be multiplied by 100/51·7, which gives 29 per cent. of arabinose; in the case of xylose, the factor would be 100/52·3. As, however, the percentage of furfuraldehyde obtained depends on the quantity of substance taken, and on other conditions, the factors are different for different cases, varying from 100/53·5 to 100/47·2 in the case of arabinose, and from 100/55·2 to 100/50·4 in the case of xylose, as the percentage of furfuraldehyde rises from 5 to 20 per cent. It must also be remembered that pentoses are not actually present in the vegetable substances, but are the products of hydrolysis of the pentosans; to calculate the percentage of the last-named substances, the percentage of the pentoses should probably be multiplied by 0·88.

In the second method, the quantity of furfuraldehyde is estimated gravimetrically, instead of volumetrically, by weighing the precipitated hydrazone after it has been washed with water and dried at 50—60°; the quantity of furfuraldehyde in the 5 grams of substance taken is obtained by multiplying the weight of the hydrazone by 0·516 and then adding 0·025 gram, which represents, on the average, the amount of furfuraldehyde in the filtrate and washings.

F. S. K.

Detection of Hydrogen Cyanide. By R. Kobert (*Chem. Centr.*, 1891, ii, 591; from *Apoth. Zeit.*, **6**, 386).—See this vol., p. 362.

Estimation of Rosin in its Mixtures with Fatty Acids. By E. Twitchell (*Analyst*, 1891, 169—171; from *J. Anal. and Appl. Chem.*, **5**, 379).—When fatty acids are dissolved in absolute alcohol and treated with hydrogen chloride, their ethereal salts are formed. Rosin treated in the same way undergoes no change. On this principle the author has based his process, which may be conducted either gravimetrically or volumetrically.

The gravimetric method is carried out as follows:—2 or 3 grams of the mixture of fatty acid and rosin is dissolved in ten times its volume of absolute alcohol, and dry hydrogen chloride is passed through in a moderate stream, the flask being placed in a vessel with water to keep it cool. The gas is rapidly absorbed, and after about 45 minutes, the ethereal salts separate and float on the solution. After waiting for half an hour longer, the liquid is diluted with five times its bulk of water and boiled until the acid solution is clear, the

ethereal salts, with rosin in solution, floating on top. To this is added some light petroleum, and the whole transferred to a separating funnel, the flask being washed out with light petroleum. The acid liquid is then run off, and the light petroleum solution washed once more with water and then treated in the funnel with a solution of 0·5 gram of potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water. The rosin is immediately saponified, and the two layers separate completely. The rosin soap solution can then be run off and the rosin recovered as usual by the addition of an acid. The first stages of the volumetric method are similar to those of the gravimetric, with the exception that the contents of the flask are washed into the separating funnel with ether instead of light petroleum, and the ethereal solution is then thoroughly washed with water until all soluble acidity is removed. 50 c.c. of neutral alcohol is then added and the solution titrated with standard solution of sodium hydroxide.

The test analyses are satisfactory. L. de K.

Estimation of Gallotannic and Gallic Acids and Tannin in Barks. By S. J. Hinsdale (*Chem. News*, **64**, 51—52; compare Abstr., 1890, 1348).—To estimate the gallotannic acid, 8 grams of the bark is extracted with boiling water, the infusion is made up to 500 c.c., and 50 c.c. of this is diluted again to 500 c.c. Five drops of the solution thus obtained is mixed with 5 c.c. of a fresh solution of ferric ferricyanide (1·5 c.c. of *liquor ferri chloridi* added to a solution of 0·04 gram of potassium ferricyanide in 500 c.c. of water); after one minute, water (20 c.c.) is added; and then, within three minutes, the colour is compared with that given by freshly-made standard tannin solution (0·008 per cent.) simultaneously treated in the same way. The solutions are so graduated that the number of drops of tannin solution required to match the colour equals the percentage of gallotannic acid in the bark. If the percentage is greater than 10, or less than 1·5, it becomes difficult to match the colour accurately, and it is therefore well in such cases to alter the strength of the infusion to the extent necessary to obtain a manageable colour.

The gallic acid is estimated in a similar way, after the precipitation of the tannin by alum and gelatin (50 c.c. of original infusion, equal to 0·8 gram of bark, 0·2 gram of alum, 20 c.c. of 3 per cent. gelatin solution, the whole made up to 250 c.c.). The colour produced by 5 drops of the filtered solution is compared with that yielded by a freshly-prepared standard solution of gallic acid, the strength of which (0·002 per cent.) is such that one-eighth of the number of drops required to match the colour equals the percentage of gallic acid in the bark.

The difference between the percentages of gallotannic and gallic acids is stated to be equal to the percentage of tannin present.

Jn. W.

The Werner-Schmid Method of Milk Analysis. By T. E. Hill (*Analyst*, 1891, 67—70).—The author was inclined to be dissatisfied with this process, as his results were anything but accurate, owing chiefly to the fluffy layer below the ether being disregarded, which consists mainly of ether mixed with a little hydrochloric acid

and decomposed caseïn. No directions for washing the ether are given. The author, however, obtained more satisfactory results by following the details of Stokes' modified process, which is as follows: —10 c.c. of the sample is measured or weighed into special tubes and mixed with 10 c.c. of strong hydrochloric acid. The mixture is boiled with frequent shaking until it turns brown, and, after cooling, ether is added up to the 50 c.c. mark. After settling for five minutes, 20 c.c. of the ether is pipetted off and evaporated in a tared dish. The number of c.c. of ether remaining in the tube is then read, together with three-fourths of a fluffy-looking stratum immediately beneath the ether, and these, added to the 20 c.c. of ether evaporated, give the total number of c.c. of ether to be considered in calculating the percentage of fat. A correction for sp. gr. has, of course, to be made in each case.

By always weighing the milk, instead of measuring, and using washed ether, and also only pipetting off 15 instead of 20 c.c., the author has succeeded in obtaining results which compared satisfactorily with those obtained by Adams' method. L. de K.

Fat Extraction from Milk Solids. By A. W. Stokes (*Analyst*, 1891, 92).—The process to be described does not lay claim to any originality, but may come in handy when an analyst has to deal with a very small quantity of a sour sample.

Five grams of the milk is dried to constant weight in a platinum, porcelain, or glass dish, and the total solids are weighed. The mass is now moistened with 5—8 c.c. of strong hydrochloric acid, and, after putting a cover-glass on the dish, heated on the top of the water-bath for three to five minutes. The contents of the dish are now well broken up with a rubber-covered glass rod and washed with water into the well-known Schmid tube.

The fat is then extracted in the usual way by shaking out with ether. L. de K.

Detection of Coco-nut Fat in Butter. By J. Muter (*Analyst*, 1891, 88—90).—Although coco-nut fat contains less volatile, fatty acids than butter fat, it is still possible to mix a comparatively large quantity of this fat with butter without seriously interfering with the popular Reichert's distillation process. On the other hand, where that excellent instrument the oleorefractometer is used, it is very easy to compound a mixture of margarin with coco-nut fat which will give the normal refraction of butter. It is, therefore, only by a joint use of the refractometer and Reichert's titration process that the fraud can be detected.

A sample of butter which has an abnormally high refraction, say, —36, must still be pronounced as pure when it gives a Reichert figure of 16 (working on 2·5 grams of butter fat), but if the refraction should be —37 and the Reichert only 12, it may be safely reported as adulterated with 20 per cent. of coco-nut fat. L. de K.

Estimation of Fat in the Products from Milk. By Lezé and Allard (*Compt. rend.*, **113**, 654—656).—A definite quantity of the

substance to be examined (cream, cheese, margarin, &c.) is placed in a flask with a graduated neck, mixed with 4 or 5 times its volume of pure hydrochloric acid, and heated at a moderate temperature with occasional agitation. The substance gradually disappears, and a liquid is obtained which becomes brown on heating. Tepid water is then added in quantity sufficient to bring the liberated fat into the neck of the flask, where it is measured (compare Abstr., 1890, 837). Pasty substances may be treated with acid in a dish and afterwards transferred to the flask with a graduated neck. A sample of Gruyère cheese gave the following percentages of fat: with ether, 31·84; with carbon bisulphide, 32·04; by the new process, 31·75. 5 grams of the cheese was treated with 50 c.c. of hydrochloric acid for 15 to 30 minutes, and heated on a water-bath until it acquired a brownish colour.

Instead of multiplying the volume found by 0·9, 9 grams of matter may be weighed out instead of 10, and the volume of the fat will then represent the percentage by weight.

The separation of the fat is complete at 25—30°, and heating on the water-bath simply serves to produce agglomeration of the fat globules. The hydrochloric acid must contain no free chlorine. The fat undergoes no chemical changes; its weight remains practically the same in a drying oven, and it leaves no ash when burned.

C. H. B.

Assay of Aconite Preparations. By A. H. Allen (*Pharm. J. Trans.* [3], **22**, 230—235).—Assuming that the physiological activity of a mixture of aconite alkaloïds is represented by the amount of saponifiable base present, the author describes a delicate and ingenious volumetric method for the determination of the latter, applicable to very minute quantities. The alkaloïd is titrated with N/50 hydrochloric acid; after hydrolysis, &c., the benzoic acid formed is determined by N/50 baryta-water, the indicators being methyl-orange and phenolphthaleïn respectively. The results adduced are fairly accordant for pure samples of aconitine and of japaconitine taken separately, and there is a presumption of the same being the case for pseudaconitine from the roots of *A. ferox*. But when the method is applied to several specimens of mixed aconite alkaloïds extracted from the root (of *A. napellus?*), the results are stated by the author to be "somewhat erratic."

In a discussion following the reading of the paper, J. C. Umney pointed out that Jürgens had shown that nearly half the alkaloïds of *A. napellus* consist of an amorphous inert base, also saponifiable and capable of yielding benzoic acid (as are aconitine and japaconitine). A gummy base in aconitine had, moreover, been noticed by Wright, Groves, and others; on all hands it was admitted that the process would be invalid if this base were proved to be capable of hydrolysis.

R. R.

General and Physical Chemistry.

Electromotive Force of Gas Batteries. By G. Markovsky (*Ann. Phys. Chem.* [2], **44**, 457—472).—The author has made measurements of the E.M.F. developed in elements consisting of platinum wholly immersed in dilute, carefully boiled-out sulphuric acid, and of platinum partially immersed in this liquid and partially exposed to an atmosphere of pure hydrogen and oxygen. Experiments were also performed when the dilute acid contained platinum sulphate in varying quantities, and in one or two instances carbon electrodes were substituted for platinum electrodes. His results are as follows:—

The electromotive force of a platinum plate in hydrogen against a platinum plate in gas-free sulphuric acid is 0·646 volt. When oxygen is substituted for hydrogen, the current is in the opposite direction and the electromotive force is 0·372 volt.

Electrolytic hydrogen, and hydrogen prepared from zinc and sulphuric acid, give the same value for the electromotive force. The same thing holds for electrolytic and chemically prepared oxygen.

The electromotive force of an oxygen cell is diminished by the addition of platinum sulphate to the solution, whilst that of a hydrogen cell increases, the sum of the two remaining constant.

The electromotive force is independent of the density and temperature (up to 70°) of the gas.

Carbon electrodes behave quite differently from platinum electrodes.

J. W.

Electrical Behaviour of Metals in Salt Solutions. By H. Pellat (*Ann. Phys. Chem.* [2], **44**, 550—554).—In this paper the author replies to objections raised by Braun against his law, that the normal difference of potential between a metal and the solution of one of its salts into which it is immersed is zero. J. W.

Electrostenolysis. By F. Braun (*Ann. Phys. Chem.* [2], **44**, 473—500).—The name "electrostenolysis" is applied by the author to the phenomenon of the decomposition of an electrolyte in a narrow crack through which a current passes (Abstr., 1891, 778). Electrostenolysis is best observed in the case of solutions of salts of heavy metals, for these metals are deposited in the crack, as on an electrode. The following substances in solution were decomposed in this way:—Silver nitrate, lead acetate, lead nitrate, auric chloride, cobalt nitrate, palladium nitrate, platinum chloride, ferrous sulphate. Salts of zinc, nickel, bismuth, the alkalis, and hydrogen showed no action. Electrostenolysis, in the case of copper salts, was only observed in ammoniacal solutions.

The material in which the crack is made seems to have no influence on the result. In order to obtain the action, the diameter of the crack and the current density must be less than a definite amount.

No electrostenolysis appears in animal or vegetable membranes, in porous cells, or in hydrophane. J. W.

Electrocapillary Reactions. By F. Braun (*Ann. Phys. Chem.* [2], 501—509).—Becquerel observed that if a crack (about 0·06 mm. in breadth) is made in a glass tube which is filled with a strong solution of sodium sulphide and dipped into a concentrated solution of cupric nitrate, metallic copper is, after some time, deposited on the edges of the crack. This is covered later by a layer of cuprous oxide, which gradually grows into the crack and may eventually burst the tube.

Ostwald has given an explanation of this phenomenon on the basis of the properties of semi-permeable membranes towards various ions (Abstr., 1890, 1355). The author, on the other hand, concludes that a galvanic element is formed by the following substances:— $CuS|Cu(NO_3)_2|$basic salt + $NaNO_3|NaHS|CuS$, which occasions the deposition of copper at the crack. J. W.

Electrolytic Preparation of Metallic Alloys, &c. By H. N. Warren (*Chem. News*, **69**, 302).—The metal to be alloyed and the compound containing the alloying element are melted together in a deep, conical crucible, having a pointed graphite rod projecting an inch through the bottom. The external portion of this rod is protected by an iron tube, coated with borax to avoid oxidation, and is connected with the negative electrode of a battery; when the mass in the crucible has become liquid, a stout platinum wire, connected with the positive electrode, is arranged so as just to touch the upper surface of the liquid, and decomposition then proceeds, the metallic ion alloying with the molten metal below. D. A. L.

Basicity of Phosphoric Acid. By D. Berthelot (*Compt. rend.*, **113**, 851—854).—When ammonia, sodium hydroxide, or potassium hydroxide is added in gradually increasing quantity to a dilute solution of phosphoric acid, the decrease in electrical conductivity is represented by a right line up to the point at which one of the basicities of the acid is neutralised, and it follows that the three monobasic phosphates are not dissociated even in dilute solutions. At this point, there is a well-marked angular deflection of the curve, but with further addition of alkali the increase in conductivity is represented by a right line up to the point corresponding with the formation of a bibasic phosphate, and it follows that the bibasic alkaline phosphates are stable, even in dilute solutions. With further addition of alkali, there is again a change in the direction of the curve, but the change of conductivity is no longer represented by a right line, and there is no change in direction at the point corresponding with the tribasic phosphate. The tribasic alkaline phosphates are almost completely dissociated in dilute solutions. With stronger solutions, it can be seen that the formation of the tribasic phosphate does correspond with a distinct, although slight, angular deflection of the curve. It is clear that phosphoric acid differs markedly from the true tribasic acids (tricarballylic, aconitic, citric, &c.), for with the latter

the monobasic and bibasic salts are partially dissociated in solution, and the tribasic salt is stable.

Lenz has shown that the salts of ammonium and potassium with strong acids show equal conductivities in dilute solution, and the author has shown that with feeble acids the two conductivities are distinctly different, although remaining approximately the same, whilst with phenol they are very different. In this paper, it is shown that the conductivities of the monobasic potassium and ammonium phosphates are identical; with the bibasic phosphates, the conductivity of the ammonium salt is about 6 per cent. lower than that of the potassium salt, whilst, with the tribasic phosphates, the two conductivities are widely different, that of the potassium salt being much the higher.

The first acid function of phosphoric acid is analogous to that of strong acids, the second to that of feeble acids, and the third to that of phenols. Phosphoric acid is, in fact, not a true tribasic acid, but a monobasic acid with a complex function. It is noteworthy that these conclusions agree with those deduced from thermochemical data.

C. H. B.

Recent Developments of the Mechanical Theory of Heat. By M. Planck (*Zeit. physikal. Chem.*, **8**, 647—656).—This report of a lecture given by the author before the German Naturforscherversammlung at Halle gives a connected account of the recent applications of thermodynamics to the study of solutions. J. W.

Thermochemistry of Bibasic Organic Acids. By G. Massol (*Compt. rend.*, **113**, 1047—1048).—The heat of neutralisation of tartaric acid with potash is +25·45 Cal. The heats of formation of various salts, calculated for the solid state throughout, are:—Potassium hydrogen succinate, 26·26 Cal.; dipotassium succinate, 46·40 Cal.; sodium hydrogen succinate, 20·19 Cal.; disodium succinate, 40·02 Cal.; dipotassium tartrate, 53·26 Cal.; sodium hydrogen tartrate, 26·01 Cal.; disodium tartrate, 45·82 Cal. From a comparison of these data with others previously given by himself (Abstr., 1891, 968, 1062; this vol., p. 260) and others (Berthelot, *Mécanique Chimique*, **1**, 539; Chroustchoff, *Ann. Chim. Phys.* [5], **19**, 422), the author concludes that the addition of alkylic hydroxyl to the carbon atom next a carbonyl group increases the heat of neutralisation, and that in the succinic series the heat of neutralisation increases with the number of alkylic hydroxyl groups; the increase, however, occurring entirely in the neutralisation of the first carbonyl group.

Jn. W.

Distillation of Coal. By P. Mahler (*Compt. rend.*, **113**, 862—864).—The sum of the heats of combustion of the products of distillation of Commentry coal was found to be 96·5 per cent. of the heat of combustion of the original coal. The following table gives the heat of combustion at constant volume of some samples of coal gas:—

	Heat of combustion per cubic metre.	Sp. gr.	Heat of combustion per kilo.
Gas made at Villette..	5601·9 Cal.	0·4033	10744 Cal.
Gas from Commentry coal.....	5804·0 „	0·4040	11111 „
Gas from Cannel coal from Niddrie.....	6365·5 „	0·6367	7735 „

C. H. B.

The Freezing Point of Isomorphous Mixtures. By F. W. Küster (*Zeit. physikal. Chem.*, 8, 577—600).—In a former paper (Abstr., 1890, 1209), the author studied the freezing points of mixtures of hexachlor-α-keto-γ-pentene and pentachlorobrom-α-keto-γ-pentene, which crystallise together in all proportions. He has now extended his observations to other pairs of isomorphous substances, and finds that in their case also the relations are similar to those already found. The freezing point, namely, does not obey Van't Hoff's law for the depression, but lies in the neighbourhood of the point calculated from the freezing points of the components by the mixture formula of simple proportion to the quantity of each present; sometimes it is a little above this point, sometimes a little below it. In the case first investigated, the solid crystallising out had the same composition as the liquid; but this is not so for all mixtures. The author gives the following rule :—In the first crop, the substance with higher melting point predominates; but if the melting points lie close together, then apparently there is a preponderance of the substance which crystallises more readily. The temperature, therefore, is not always constant, but gradually diminishes.

The isomorphous mixtures investigated were metachloronitrobenzene and metabromonitrobenzene, trichloracetamide and tribromacetamide, α-chlorocinnamaldehyde and α-bromocinnamaldehyde, chloroquinol diacetate and bromoquinol diacetate. Mixtures of naphthalene and dihydronaphthalene were also studied, although these substances are probably not isomorphous. Acetanilide and paranitracetanilide when melted together do not crystallise homogeneously, and the freezing point very nearly obeys Van't Hoff's law. Their isomorphism is somewhat doubtful. J. W.

Pressure of Saturated Water Vapour. By G. Hinrichs (*Zeit. physikal. Chem.*, 8, 680—681).—The author points out that the results recently obtained by Cailletet and Colardeau agree with the values calculated from his theoretical formula for the vapour pressure of water. J. W.

Vapour Tension of Homologous Compounds. By G. C. Schmidt (*Zeit. physikal. Chem.*, 8, 620—646; compare Abstr., 1891, 969).—The author has made measurements of the vapour pressure of the alcohols of the fatty series at various temperatures. He finds that Dalton's rule is not verified, as may be seen from the following tabulation of his results :—

	Boiling points for the pressure in mm.									
	1600.	Δ.	1000.	Δ.	400	Δ.	100.	Δ.	10.	Δ.
Methyl alcohol...	87·8		74·3		51·3		22·6		−14·6	
Ethyl „ ...	98·4	10·6	85·4	11·1	62·9	11·6	34·5	11·9	− 2·5	12·1
Propyl „ ...	118·7	20·3	104·6	19·2	80·8	17·9	51·4	16·9	13·6	16·1
Isobutyl „ ...	128·9	10·2	114·8	10·2	90·8	10·0	60·7	9·3	21·5	7·9
Isoamyl „ ...	154·7	25·8	139·0	24·2	112·9	22·1	81·2	20·5	41·0	19·5

J. W.

Rapid Method of Solution in the Cold. By J. B. Coleman (*J. Soc. Chem. Ind.*, **10**, 231—233).—The author found that by simply passing a current of air through the coarsely powdered solid suspended in water complete solution is obtained, in some cases in the space of 15 minutes, and in most cases before the expiration of an hour. The solid is put into a glass cylinder half filled with distilled water. The mouth of the jar is tightly stoppered with an india-rubber cork through which pass two glass tubes. One tube has inserted in the upper end a plug of cotton wool to keep out dust, whilst the lower end is drawn out and bent, and passes to the bottom of the cylinder; the other tube just passes through the cork. Before use, the cylinder is surrounded by a vessel containing water of the temperature at which the solubility is to be taken; the short tube is then connected with a water aspirator. The advantages of this process consist in the comparatively short time required for solution, and in the circumstance that no expensive apparatus, such as water motors and revolving agitators, are required. In places where high-pressure water is not available, steam may be substituted by attaching a flask of boiling water to the aspirator. The objections to the process are that the solution may be supersaturated by the air causing evaporation during its passage through the liquid; and, secondly, that readily oxidisable substances cannot be examined in this way. The first objection may be overcome by the use of moist air, whilst the second difficulty can usually be met by employing coal gas in place of air, care being taken that the oxygen and carbonic anhydride present in the gas are thoroughly absorbed by alkaline pyrogallol solution. D. B.

Analogies between Solutions of a Gas and of a Salt in an Indifferent Salt Solution. By J. Setschenow (*Zeit. physikal. Chem.*, **8**, 657—660).—The author finds from Bodländer's numbers (Abstr., 1891, 795) that the solubility of one salt in the solution of another indifferent salt obeys the same law as he had observed to hold good for the solubility of carbonic anhydride in salt solutions, provided the concentration of the solution is not too great.

J. W.

State of Salts in Solution: Sodium Sulphate and Strontium Chloride. By A. Étard (*Compt. rend.*, **113**, 854—857).—It is well

known that the solubility of sodium sulphate increases from 0° to 33°, at which point the saturated solution contains 34·5 per cent. of the anhydrous salt. As the temperature rises, the solubility decreases, and part of the sulphate separates in an anhydrous form. According to Tilden and Shenstone, the solubility attains another minimum at 130°, and then again increases. The author finds that the solubility decreases from 33° to 80°, the percentage of anhydrous sulphate in a saturated solution at the latter temperature being 30·0 per cent. Beyond this point, the solubility remains constant up to 230°, the composition of the solution corresponding with the formula $Na_2SO_4 + 18H_2O$. Beyond 230°, the solubility rapidly decreases, and a solution saturated at 320° contains only 17·8 per cent. of the salt.

There is no proof that when a hydrated salt is dissolved in water a solution of the particular hydrate is formed; there may be interaction between the solvent and the salt, with formation of hydrates of different composition.

The author has redetermined the solubility of strontium chloride, $SrCl_2 + 6H_2O$. Between −15° and 40°, the solubility increases, and is represented by a right line; then the rate of increase of solubility changes, the curve becomes convex towards the axis of temperature, and a maximum is reached at 61°. Beyond this point, the solubility decreases up to 80°, the curve being convex towards the axis of temperature, and, between 80° and 250°, the solubility is represented by a right line. The cause of the perturbation between 40° and 80° is easily established. Below 40°, the solution deposits only needles of the composition $SrCl_2 + 6H_2O$: between 90° and 130°, it deposits lamellæ of the hydrate $SrCl_2 + 2H_2O$; at 75°, it deposits both needles and lamellæ. At 145°, a saturated solution deposits needles, probably of a monohydrate, and then lamellæ of the dihydrate, and the right line represents the sum of the solubility of the two hydrates.

C. H. B.

Supersaturation. By L. de Boisbaudran (*Compt. rend.*, **113**, 832—835).—The author quotes certain passages from a paper read before the Academy in 1866, but not previously published. Supersaturation is a general phenomenon common to all substances, superfusion being essential to the crystallisation of a fused substance, and supersaturation of a vapour to the crystallisation of a sublimed substance. Each change can take place at various temperatures, two of which are especially noteworthy and limit the phenomenon. The change of state takes place at the higher limit if the change is inverse, and at the lower limit if the change is direct, only when the substance is in contact with some of the product of the change of state or an analogous product capable of mixing with it intimately. The term *direct* change denotes the fusion of a solid or the volatilisation of a liquid; whilst the term *inverse* change denotes the condensation of a gas or the solidification of a liquid. Crystallisation will take place at the higher temperature limit only when the liquid is in presence of previously-formed crystals of the same substance, or some isomorphous substance. Condensation will take place at the higher temperature limit only when the gas is in contact with some of the product formed by previous condensation or some liquid capable of

mixing intimately with it. Both these changes will, however, take place at the lower temperature limit, even in absence of products of the change or analogous substances. Similar phenomena are observed in the case of the inverse changes, except that it is at the higher temperature limit that the change will take place in absence of products of the change. In the author's view, substances that mix intimately or dissolve in one another, may be regarded as isomorphous, or approximately isomorphous; but, as shown in 1875, this isomorphism no longer exists when the lower limit of supersaturation is reached.

C. H. B.

Velocity of the Reaction between Alcoholic Potash and Alkyl Halides, &c. By M. Wildermann and S. Aisinmann (*Zeit. physikal. Chem.*, **8**, 661—676).—The authors investigated the rate at which hydrogen halide was split off from the halogen derivatives of the fatty hydrocarbons by alcoholic potash. They found that the coefficient of velocity, C, is greatest for iodides and least for chlorides.

	C.	
(*a.*) Ethyl iodide	0·00162	(38·5°)
„ bromide	0·00092	(39°)
(*b.*) Propyl iodide	0·00051	(38·5°)
„ bromide	0·00022	(39°)
(*c.*) Ethylene bromide.....	0·00120	(18°)
„ chloride.....	0·00017	(40°)

The constant for the removal of the first halogen atom from a dihalogen derivative is greater than the constant for the corresponding mono-halogen derivative, thus:

Propyl bromide	C = 0·00022 at 39°
Propylene bromide	C = 0·00084 at 18°

although the constant increases with the temperature. The constant is less for unsaturated than for saturated derivatives. J. W.

Molecular Dissymmetry. By P. A. Guye (*Chem. Centr.*, 1891, ii, 909—912).—Pasteur has shown that all chemical compounds may be divided into two classes: those with dissymmetrical and those with homohedral arrangement of the atoms in the molecule. The first includes all optically active substances, and to every dextrorotatory there is a corresponding lævorotatory variety. The tetrahedron representing any asymmetrical carbon atom CRR′R″R‴ may have either dextro- or lævo-dissymmetry. If the masses of RR′R″R‴ are nearly equal, the dissymmetry of the molecule will be much smaller than if the masses are very different; so that in the first case the optical activity will be almost nothing; but in the second it will be large. The optical activity is therefore a measure of the dissymmetry of the molecule. Any expression of the dissymmetry must fulfil these two conditions: that its value is *nil* when the carbon atom is symmetrical, and that it changes sign with the passage from dextro- to lævo-symmetry. An asymmetrical tetrahedron has no plane of symmetry; but a symmetrical one has several: six for the

compound CR_4, three for $CR'R_3$, and one for $CR'R''R_2$. As long as the carbon atom is symmetrical, the centre of gravity will lie in one of the above six planes, but, as soon as it becomes asymmetrical, the centre of gravity will lie out of these planes. If the distance of the centre from each of the planes is denoted by d_1, d_2, d_3, d_4, d_5 d_6, the product P of these distances is a measure of the dissymmetry of the tetrahedron, and, consequently, of the optical activity.

The factors d_1, d_2, &c., will have the positive or negative sign, according to the side of the plane of symmetry on which they lie. If one of the factors becomes nothing, P will be nothing, and the carbon atom becomes symmetrical. With regard to the position of the centre of gravity, it will be necessary to assume either that the masses $RR'R''R'''$ are concentrated at the angles of the tetrahedron or not. The distances of the centres of gravity of these masses from that of the tetrahedron may be estimated from the theories with regard to the molecular volume. The molecular refraction is proportional to the spherical volume of the molecule, and is also made up of the sum of the atomic refractions. The square root of the atomic refraction gives, therefore, a number which may be termed the atomic diameter, and which represents the mean sphere of action of the atom. By thus obtaining values for the relative distances of $RR'R''R'''$ from the centre of gravity of the tetrahedron, it is possible to estimate the position of the latter with regard to the planes of symmetry. If by the substitution of one element or radicle for another in the molecule of an active substance, the centre of gravity remains on the same side of the planes of symmetry, the optical rotation of the new product will be of the same sign as that of the parent substance. If the position of the centre of gravity with regard to the planes of symmetry changes, the sign of the rotation will also change. The author quotes experimental evidence in support of these theories.

H. C.

Levelling Instrument for Gasometric Investigations. By G. Lunge (*Ber.*, **24**, 3948—3949).—In gasometric investigations it is frequently necessary to place the tops of two mercury columns at the same level; this end may sometimes be attained by aligning them against the top of a roof, wall, or similar horizontal object. In many cases, however, such an object is not available, and the author has, therefore, devised a little instrument by means of which the levelling may be readily carried out. It consists of a brass rule, to the front of which a small spirit level is attached, and to the back a long brass rod, which passes accurately into a brass tube, the end of which can be fixed on a retort stand in the same manner as an ordinary retort-stand ring. This is then placed on the stand holding the gas-measuring tubes, and, after the mercury columns have been approximately levelled, is raised to about the same height, and the rule moved until the spirit level shows it to be exactly horizontal; the tops of the two columns can then be readily levelled by a comparison with the upper edge of the brass rule. H. G. C.

New Condenser for Laboratory Purposes. By F. Evers (*Ber.*, **24**, 3950—3951).—The condenser described by the author is a

modification of the ordinary Liebig's condenser, in which the inner tube is replaced by a cylinder of moderate width, containing within it a third narrower cylinder. The latter is connected by means of small transverse tubes with the space between the second and first cylinders, thus enabling the tap-water to cool the opposed surfaces of the two inner cylinders. A very great increase is thus obtained in the extent of cold surface to which the vapours passing the condenser are exposed, without materially increasing the dimensions of the condenser itself. H. G. C.

Lecture Experiment: Dissociation of Phosphonium Bromide. By G. S. Newth (*Chem. News*, **64**, 301).—A Liebig's condenser in miniature is constructed, in which the inner tube consists of a tobacco pipe (or pieces of tobacco piping joined with rubber tube), fixed by small pieces of rubber tube into an outer glass tube 30 cm. long and 10 mm. bore. A stream of hydrogen is passed into one of the side tubes of this glass tube, and is burnt at a fish-tail burner screwed into lead pipe and attached to the other side tube. A small U-tube, containing phosphonium bromide, is connected to one end of the clay pipe, then, almost as soon as a slow stream of hydrogen is passed (especially if the U-tube is warmed by the hand), the flame of the hydrogen indicates the presence of phosphorus, due to the diffusion through the clay pipe of the hydrogen phosphide arising from the dissociation of the phosphonium bromide, whilst the acidity of the gas issuing from the end of the clay pipe is due to the hydrogen bromide, the other product of the decomposition. D. A. L.

Inorganic Chemistry.

Direct Combination of Chlorine with Metals. By U. Kreusler (*Ber.* **24**, 3947—3948).—The author has observed that if in the well-known experiment of burning a spiral of thin brass wire tipped with Dutch metal in chlorine gas, the latter be dried, no combustion takes place, but that the addition of a little moisture brings about an immediate combination. The simple drying brought about by passing the gas through a single flask of sulphuric acid is quite sufficient to prevent the combustion taking place. H. G. C.

Note.—The fact that dry chlorine does not act on Dutch metal and other metals was shown some time ago by Cowper (Trans., 1883, 154). —Ed.

Sulphuryl Holoxide. By M. Traube (*Ber.* **25**, 95—97; see also Abstr., 1891, 978).—The paper is an answer to the criticisms of Berthelot (*Compt. rend.*, **112**, 1481) and Marshall (Trans., 1891, 771). The author has repeated the experiments formerly described, and maintains the existence of the compound SO_4. E. C. R.

Free Hydroxylamine. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **10**, 100—112).—This note has been published by the author in consequence of the appearance of a paper by Meyer on the stability of hydroxylamine (*Annalen*, **264**, 126). Lossen's experiments were all made in presence of water. The author considered that the presence of the water may, at least, have favoured the decomposition of the hydroxylamine, if it were not even the prime cause of the want of success attending the efforts to isolate that substance. As hydroxylamine hydrochloride is more soluble in methyl alcohol than in ethyl alcohol, absolute methyl alcohol has been employed as solvent.

The first preparations made showed that hydroxylamine is not a gas, and that a dilute solution in methyl alcohol becomes more concentrated by spontaneous evaporation in the air.

Further attempts to prepare larger quantities of material resulted in the explosion of the residue after the methyl alcohol, together with a small proportion of hydroxylamine, had been distilled off at atmospheric pressure.

The method of preparation finally adopted was as follows:—100 grams of hydroxylamine hydrochloride was dissolved in 600 c.c. of absolute methyl alcohol at a gentle heat. The calculated quantity (to leave the hydrochloride in slight excess) of a titrated concentrated solution of sodium methoxide was then added while the solution was still hot, the sodium chloride filtered off, and the filtrate distilled at a pressure of 160—200 mm. The alcohol carried over less hydroxylamine at this reduced pressure. When most of the alcohol had distilled over, dry ether was added to the residue; this separated into two layers, the upper containing 5·5 per cent. of hydroxylamine, and the lower 53·5 per cent.

A portion of the lower layer was separately distilled under a pressure of 165 mm., until a temperature of 86° was reached; the residue contained 70 per cent. of free hydroxylamine.

After an interval of six weeks, during which some decomposition took place, all the solutions were mixed and distilled under a pressure of 60 mm. The first portions of the distillate contained ammonia and methyl alcohol; then a fraction containing 32 per cent. of hydroxylamine was collected. The residue, containing 80 per cent. of free hydroxylamine, was fractionally separated into three parts. The first contained 27·2, the second 60 per cent. of hydroxylamine. The last portion solidified in the cooled receiver, forming long needles. The last part of this passed over at 70° under 60 mm. pressure. The solid substance, after pressing twice between filter paper, gave a hard, crystalline mass, containing 99·4 per cent. of free hydroxylamine. Free hydroxylamine is a very hygroscopic substance which rapidly liquefies in the air. The melting point was ascertained, by placing a thermometer in the melting crystals, to be 27·5°; for the pure substance, it is somewhat higher, the sample used had been prepared some hours, and kept in a badly stoppered bottle.

Sodium chloride is readily dissolved by hydroxylamine, and powdered potassium nitrate liquefies the solid. In these properties it resembles water (ice). Sodium attacks the solid violently. Free

hydroxylamine is inodorous, and rather denser than water. When heated rapidly on platinum foil, it explodes with a fine, clear, yellow flame. It dissolves very little, or not at all, in chloroform, benzene, ether, ethyl acetate, or carbon bisulphide; with carbon bisulphide, it, however, reacts with the separation of sulphur. Exposed to the air, it first liquefies, and then disappears by evaporation. It acts to some extent on paper and cork. The pure substance appears to be stable, as are certainly its concentrated aqueous solutions free from salts. Hydroxylamine, when melted, forms a rather thick liquid. Its dilute aqueous solutions remain stable at a high temperature. The 60 per cent. solution shaken with methyl iodide and methyl alcohol forms a white, crystalline mass after some hours. Bromine and iodine attack it with great violence. W. T.

Reduction of Nitric Acid to Ammonia by the Galvanic Current. By A. Becker (*Chem. Zeit.*, **14**, 1557).—Vortmann's recent process for the quantitative estimation of nitric acid by electrolysis is, according to the author, based on the formation of a hydrogen alloy.

Vortmann electrolyses the nitrate in presence of sulphuric acid and a metallic salt, such as cupric sulphate. During the electrolysis, metallic copper is deposited, and hydrogen is evolved, but neither of these are capable of effecting the reduction. As there is, however, in Vortmann's process, no doubt about the reduction, the author concludes this is caused by an alloy of copper and hydrogen. In his opinion, the reduction would take place instantaneously in presence of the compound of palladium and hydrogen. L. de K.

Some Hypophosphates. By C. Rammelsberg (*Chem. Centr.*, 1891, ii, 790; from *Math. Naturwiss. Mitt. Sitz. Akad. Wiss. Berlin*, 1891, 369—376).—*Lithium hypophosphate*, $2Li_2PO_3,7H_2O$, is obtained as a crystalline precipitate when a solution of lithium chloride is mixed with a solution of sodium hypophosphate. It dissolves in 120 parts of water, and may be obtained in lustrous crystals of the above composition if crystallised from acetic acid solution. 5 mols. H_2O are separated at 120°, and 6 mols. H_2O at 200°. The same salt is obtained if lithium carbonate be added to hypophosphoric acid in such quantity as to leave the solution strongly acid, whilst from the mother liquor the acid salt, *lithium hydrogen hypophosphate*, $LiHPO_3 + H_2O$, may be obtained in hygroscopic crystals.

Thallium hypophosphate, Tl_2PO_3, is obtained by neutralising the hot solution of hypophosphoric acid with thallium carbonate. It separates as slender, silky needles. The *acid salt*, $2TlHPO_3,Tl_2PO_3$, is obtained by adding half the quantity of thallium carbonate. It forms small, lustrous crystals.

Barium hypophosphate, $BaPO_3$, is precipitated from the solution in acids by the addition of ammonia. After drying over sulphuric acid, it still retains 1·62 per cent. of water. If the neutral salt be dissolved in hydrochloric acid and the solution allowed to evaporate, the acid salt, $BaH_2(PO_3)_2 + 2H_2O$, crystallises out; it loses the water of combination at 200°.

Magnesinm hypophosphate, $MgPO_3 + 6H_2O$, is obtained as a fine, crystalline precipitate when normal sodium hypophosphate is added to a solution of magnesium sulphate; it is sparingly soluble. If heated with acetic acid and a little hydrochloric acid, it dissolves, and the salt $MgPO_3 + 12H_2O$ is obtained from the solution by concentration; 6 mols. H_2O separate at 200°. An acid magnesium salt could not be obtained.

Beryllium hypophosphate, $2BePO_3 + 3H_2O$, is obtained as a precipitate by adding a hot solution of beryllium sulphate to a solution of sodium hypophosphate; at 230—250°, about half the combined water separates.

When heated, the anhydrous hypophosphates are resolved into a mixture of phosphide and pyrophosphate, according to the equation $7R''PO_3 = 3R''_2P_2O_7 + R''P$. The change occurred quantitatively in the case of the silver salt. The lead and barium salts, after drying at 200°, still retained some water, and, consequently, when heated, small quantities of phosphorus and hydrogen phosphide separated from them. J. W. L.

Metallic Borates. By H. Le Chatelier (*Compt. rend.*, **113**, 1034—1036).—The author considers that many compounds of boric acid, such as fused borax, which are usually regarded as definite salts, are really mixtures, and that all known metallic borates may be looked on as salts of orthoboric or metaboric acid. It is possible to include the natural calcium borates, colemanite and perseïte, as well as the acid salts, such as borax, in this classification, by regarding part of the water of crystallisation as an essential constituent of the salt, a view which is justified by the tenacity with which this water is held.

A re-examination of the compounds prepared by Ebelmen, and described by Mallard (*Ann. des Mines*, 1887), has resulted in their resolution into constituents in a manner according with these views; *trimagnesium orthoborate*, $Mg_3B_2O_6$, can, for example, be isolated by means of methylene iodide or boiling water from the melts obtained by fusing magnesia with boric anhydride in various proportions. That the clean and uniform appearance of crystals is no criterion of purity was shown by fusing zinc oxide with boric anhydride in proportions varying from 1·5 to 2·75 mols.; the crystals obtained, although apparently homogeneous, were invariably found to be coated with a thin, transparent layer of boric anhydride. *Trizincic orthoborate*, $Zn_3B_2O_6$, crystallises in rhomboïdal dodecahedra, and can be easily separated from the melt by means of mineral acids, in which it is insoluble. *Calcium metaborate*, $CaBO_2$, is prepared by immersing a fragment of boric anhydride in a mixture of calcium chloride and alkali chloride, which is fused and exposed to moist air in an open crucible. Jn. W.

Silicon Thiochloride. By A. Besson (*Compt. rend.*, **113**, 1040—1041).—The reaction which results in the production of silicon chloride and sulphur from sulphur dichloride and silicon at a temperature below redness extends at a higher temperature to the

formation of silicon thiochloride. A current of chlorine saturated with sulphur dichloride vapour is led over a quantity of crystalline silicon heated to bright redness in a porcelain tube, the silicon sulphide which rapidly chokes the tube being removed from time to time by allowing the chlorine to pass alone. The liquid product is fractionated from excess of sulphur chloride, and is purified from oxychloride by recrystallisation from carbon tetrachloride, and subsequent sublimation in a current of dry air at 100°.

Silicon thiochloride, $SiSCl_2$, is a white solid which crystallises in white needles, melts at 74°, and boils at 185°. It is unstable in moist air, and is violently decomposed by water with the formation of hydrogen sulphide and chloride, and silica. JN. W.

Allotropic States of some Elements. By E. PETERSEN (*Zeit. physikal. Chem.*, **8**, 601—623).—The object of this investigation was to determine the relation between the changes of volume and of energy in passing from one allotropic modification of an element to another. True allotropic varieties differ, according to the author, in

	Heat of oxidation.	Atomic volume.
Carbon—	(C,O_2).	
α. Amorphous	965·3—969·8	6·7—8·0
β. Graphite	933·6	5·3
γ. Diamond	932·4—945·5	3·4
Arsenic—	(As_2,O_3)	
α. Steel-gray, rhombohedric	1568·3	13·1
β. Grayish-black, amorphous	1548·4	15·94
γ. Brown amorphous	1635·0	15·99
Sulphur—	(S,O_2)	
α. Rhombic, sol. in CS_2	710·8	15·9
β. Monoclinic, sol. in CS_2	717·2	16·4
γ. Amorphous, insol. in CS_2	719·9	17·1
Selenium—	(Se,O_2)	
α. Amorphous, sol. in CS_2	572·5	18·4
β. Monoclinic, ,,	562·0	17·7
γ. Crystalline, insol. in CS_2	558·2	16·5
Silver—	(Ag_2,O)	
α. Precipitated by Cu	59·0	10·3
β. ,, $FeSO_4$	124·7	10·3
Gold—	($Au_2O_3,3H_2O$)	
α. From $AuCl_3$, light-coloured	−131·9	10·17
β. From $AuHBr_4$, dark-coloured	−67·7	10·14
γ. From AuBr, metallic lustre	−37·9	10·00
Phosphorus—	(P_2O_5,Ag)	
α. Yellow	$\alpha-\beta>100$	17·0
β. Red		14·7

the quantity of energy they contain, in specific gravity, in specific heat, and in solubility. Colour and crystalline form he considers of secondary importance.

His results are summed up in the preceding table (p. 405):—

On the basis of these results, the author divides the various cases of allotropy into three groups:—

Group I.—The transition from one modification to another is accompanied by a contraction and a slight evolution of heat. To this group belong the modifications of sulphur and selenium.

Group II.—The heat evolution is considerable, and accompanied by a change of volume. Phosphorus and arsenic, crystalline and amorphous carbon, are examples.

Group III.—The thermal effect is accompanied by no change of volume. Gold and silver are examples. J. W.

Graphite. By W. Luzi (*Ber.*, **24**, 4085—4095).—It has been observed by Schafhäul, Marchand, and Brodie that, when finely-pulverised graphite is boiled with concentrated sulphuric acid, a mixture of sulphuric and nitric acids, sulphuric acid and potassium dichromate, or sulphuric acid and potassium chlorate, and subsequently washed and ignited, it swells up and assumes a characteristic vermiform or moss-like appearance. The author finds that concentrated nitric acid, or a solution of potassium permanganate in sulphuric acid, also effects the change, which likewise takes place when the coarsely pulverised graphite is simply moistened with concentrated, red, fuming nitric acid, and ignited in a flame on platinum foil, worm-like forms being obtained in this way, 2 cm. in circumference and 15 cm. in length; they are capable of being pressed into any form, are extremely light, and float upon water, alcohol, and ether. In the inner portions of these masses, lamellar crystals are found which have a brown or greenish appearance under the microscope in reflected light. In continuing his experiments, the author found that certain specimens of graphite do not undergo this change; graphites may, therefore, be divided into two groups, according as they do or do not exhibit this phenomenon, which he designates the "nitric acid reaction." Rocks containing graphite may be examined by this method with the aid of the microscope to determine to which group their graphite belongs. A mixture of the two kinds of graphite may be separated, after treatment with nitric acid and ignition, by adding the product to water, when that which remains unchanged sinks to the bottom, whilst the modified graphite floats upon the surface.

The author is unable to offer any explanation as to this difference of behaviour, as all the specimens of the two groups experimented with were morphologically identical, and, so far as could be ascertained, had the same specific gravity; they were also practically pure. Those specimens giving the "nitric acid reaction" contained, for the most part, large crystals, and it is proposed to retain the name graphite for such as these, reserving that of "graphitite" for the others.

According to the author, molten silicates serve as crystallisation

menstrua for carbon; better results are obtained, however, by mixing the silicates with a fluoride and some water, thus:—When potassium silicate (2 parts) and fluorspar (1 part) is pulverised with so much amorphous carbon that the mixture is of a mouse-grey colour, moistened with water, and heated in a well-closed porcelain crucible under a clay hood with the blast lamp for about three quarters of an hour, and slowly cooled down, graphite-like crystals are formed. The same result is obtained by fusing together a mixture, moistened with water, of sodium silicate (6 grams), colourless fluorspar (3·5 grams), and soot from a luminous gas flame. The last-mentioned discovery appears to throw light on the natural formation of graphite by contact metamorphosis (Beck and Luzi, Abstr., 1891, 989).

A. R. L.

Analysis of the Products of Incomplete Combustion. By V. B. Lewes (*J. Soc. Chem. Ind.*, **10**, 413—417).—In this paper, a successful attempt has been made to utilise the property which finely divided palladium has, of causing the oxidation of hydrogen, but not of methane, when a mixture of these gases with air is passed over it, experiments having shown that a separation between these gases is possible, owing to the fact that the carbonic oxide is oxidised into carbonic anhydride under the same conditions. For the combustion of hydrogen, palladium asbestos was used, the gas being passed through a small, V-shaped combustion tube, 10 inches in length, containing the palladium asbestos, and heated in a bath of melted paraffin wax at 200—220°. This arrangement was employed for the determination of the composition of the gases escaping into the atmosphere when the flame of an atmospheric burner is brought into contact with the bottom of a vessel, which is kept cool by water between 0° and 100°. The experiments, which are described in detail in the paper, show that the extreme tip of an atmospheric burner is the only portion of a flame which can be utilised for heating substances cooler than itself without giving rise to deleterious products of incomplete combustion, this circumstance being confirmed by analyses of the gases escaping unburnt from the outer zone of a luminous flame and an atmospheric burner flame respectively. It is further shown that the air mixed with coal gas in an atmospheric burner produces a far more complete combustion than in the case of a luminous flame, where the air, mixing with the partially burnt coal gas, so dilutes it and cools it down at the edge of the flame, that large quantities of even the inflammable hydrogen escape unburnt. In the analyses of the products of incomplete combustion, the large proportion of carbonic oxide in the outer tip of the luminous flame is due to the reduction of carbonic anhydride by the deposit of red-hot carbon on the bottom of the vessel.

D. B.

Calcium Phosphate from Solution in Acetic Acid. By H. E. Davies (*Chem. News*, **64**, 287).—Bright, glittering, prismatic crystals, giving, on analysis, numbers corresponding with the formula CaH_5PO_6, are obtained by slow crystallisation from solutions of freshly-precipitated tricalcium phosphate in acetic acid. The fact that these crystals only lose water at high temperatures, and not at 100°, is accepted by

the author as indicating absence of water of crystallisation, and the compound is therefore regarded as a derivative of phosphorus penthydroxide, of the formula $P(OH)_4 \cdot O \cdot Ca \cdot OH$. D. A. L.

Action of Carbonic Anhydride and Ferric Hydroxide on Tricalcium Phosphate. By G. v. Georgievics (*Monatsh.*, **12**, 566—581).—When carbonic anhydride is passed through water containing tricalcium phosphate in suspension, some of the calcium is withdrawn by it to form calcium carbonate, whilst dicalcium hydrogen phosphate is simultaneously produced. At the same time, a portion of the tricalcium phosphate appears to dissolve as such in the solution of hydrogen calcium carbonate which results from the presence of a large excess of carbonic anhydride.

Freshly precipitated ferric hydroxide in presence of carbonic anhydride is capable of withdrawing phosphoric acid from tricalcium phosphate, and under certain circumstances, namely, the presence of a sufficiently large proportion of the hydroxide and carbonic anhydride, the reaction becomes quantitative. G. T. M.

Action of Barium Peroxide on Metallic Salts. By H. Kwasnik (*Ber.*, **25**, 67—70).—Kassner has observed (Abstr., 1891, 245) that barium peroxide is acted on by potassium ferricyanide with evolution of the whole of the oxygen and formation of potassium ferrocyanide, the oxygen being free from ozone or hydrogen peroxide. The author then observed that ferric chloride also causes a copious evolution of oxygen from barium peroxide, but that in this case no reduction to ferrous salt takes place, only half the total oxygen being evolved, according to the equation

$$6BaO_2 + 4FeCl_3 + 6H_2O = 3O_2 + 4Fe(OH)_3 + 6BaCl_2.$$

Here also the oxygen evolved is free from ozone and hydrogen peroxide.

All ferric salts have the same action on the peroxide, and likewise the ferrous salts, these being first oxidised to ferric salts. The salts of potassium, sodium, lithium, ammonium, calcium, strontium, and barium are without action; magnesium salts give a reaction after some time; zinc and cadmium salts more rapidly; whilst those of nickel and cobalt give an immediate evolution of gas, the solutions assuming the colour of the hydroxides. Manganese, aluminium, chromium, and copper salts behave in a manner similar to the ferric salts. The salts of mercury, silver, and gold are reduced to the metallic state, with evolution of all the oxygen in the form of gas; a solution of chloroplatinic acid, on the other hand, although it causes the evolution of oxygen, does not yield metallic platinum, but unites with the barium, forming barium platinochloride. If silver nitrate be added to the solution of chloroplatinic acid, a precipitate of silver chloride and silver platinochloride is formed, and platinic chloride remains in solution; this mixture, on treatment with barium peroxide, gives a mixture of metallic silver and platinum. The reduction of the insoluble silver chloride led the author to examine the action of barium peroxide on other insoluble salts, and it was found that the reaction takes place readily with various insoluble sulphates, carbonates, phosphates, and arsenates. H. G. C.

Magnesium Nitride. By V. Merz (*Ber.*, **24**, 3940—3944).—It has been shown by Briegleb and Geuther (*Annalen*, **123**, 228) that magnesium filings are converted into magnesium nitride, Mg_3N_2, by strong ignition in a current of nitrogen. The author finds that the combination may be readily demonstrated in the following manner:—1·5—2 grams of well-dried magnesium powder is introduced into an eprouvette of hard glass, about 20 cm. in length and 12—13 mm. in diameter, which is connected on one side with a long tube passing vertically downwards and dipping under coloured water, and on the other hand with an apparatus for the preparation of pure and dry nitrogen. As soon as the air is completely driven out by nitrogen, the magnesium is heated by two or three large Bunsen burners, and, after two or three minutes, the current of nitrogen stopped by means of a pinch-cock. The water is then observed to rise rapidly in the vertical tube, and attains a height of about 3 metres in 2—3 minutes; the gas may then be again passed into the apparatus, and the absorption repeated several times. After an ignition of 40—60 minutes, almost the whole of the magnesium is converted into the nitride, the remainder having acted on the glass, blackening it, owing to the formation of silicon. The magnesium nitride thus obtained may be readily detached from the glass, and forms a light, loosely aggregated, pale-yellow, brittle mass, which has generally a greenish-grey tinge, and sometimes shows an orange surface colour; on warming, it assumes first a darker yellow colour, and then becomes reddish-brown, or brick-red, if in the form of powder. The moisture of the air rapidly decomposes it, with evolution of ammonia and formation of magnesium hydroxide; on treatment with a small quantity of water, it behaves in a very similar manner to quicklime, whilst, with a larger quantity of water in a flask, the ammonia is evolved almost explosively. The evolution of ammonia with water may also be shown with the mixture of magnesia and magnesium nitride prepared by burning magnesium in a limited supply of air.

Briegleb and Geuther state that magnesium and ammonia only act on one another at temperatures which cause a dissociation of the latter into its elements; the author finds, however, that magnesium powder readily withdraws the nitrogen from ammonia at a much lower temperature. Thus, when 1 to 1·25 grams of magnesium powder is heated with a single Bunsen burner in a current of ammonia gas, thoroughly dried and free from air, a sudden ignition is observed, which rapidly spreads through the whole mass, a gas being simultaneously evolved which has all the properties of hydrogen. It was found that after 15—20 minutes' ignition, about 90 per cent. of the magnesium had been converted into the nitride, the remainder having acted on the glass with formation of silicon. By this method, much larger quantities of the nitride may be prepared without difficulty.

The formula Mg_3N_2 requires 28 per cent. of nitrogen; the samples prepared by the above methods gave, in the best instances, 24·8, 25·2, and 25·3 per cent. H. G. C.

Supposed Copper Nitride. By P. L. Aslanoglou (*Chem. News*, **64**, 313).—Grove stated, in 1841, that a nitride of copper, sp. gr. 5·9,

was produced by the action of an electric current when metallic copper forming the positive electrode and platinum the negative electrode were immersed in a solution of ammonium chloride. The author, having repeated the experiment many times, finds that the product has a specific gravity of 5·6, that it does not contain nitrogen, but really consists of cuprous oxide and metallic copper in the proportions of Cu_2O + Cu. D. A. L.

Copper Phosphides. By Granger (*Compt. rend.*, **113**, 1041—1042).—The product which Abel obtained as a hard, brittle, steel-grey mass by passing phosphorus vapour over red-hot copper, is not a pure substance, but it may be converted into a crystalline phosphide by repetition of the treatment. *Pentacupric diphosphide*, Cu_5P_2, crystallises in bright, steel-grey, hard, brittle, hexagonal prisms, of which the crystallographic data are given. It dissolves easily in hot nitric acid. When heated to dull redness in air, it is oxidised to copper phosphate, but if the air is replaced by an inert gas, phosphorus is given off, and a residue of *tricuprous phosphide*, Cu_3P, is left; at a higher temperature, however, still more phosphorus is lost.

Jn. W.

Chemical Changes between Lead and Nitric Acid. By V. H. Veley (*J. Soc. Chem. Ind.*, **10**, 206—210).—The main conclusions to be drawn from the experiments described by the author are briefly summed up as follows:—(1) The behaviour of lead towards nitric acid is different, except in the production of nitrous acid, from that of silver, mercury, copper, and bismuth; (2) lead is attacked less by very dilute or by concentrated nitric acid than by an acid of intermediate strength; (3) lead is attacked less by nitric or nitrous acid taken separately than by mixtures of the two acids, the action in the latter case being greater the more nearly equal is the proportion between the nitric and nitrous acids; (4) in constructing vessels through which nitric acid or mixtures of nitrous and nitric acids might pass, no advantage appears to be obtained by alloying the lead with small portions of antimony. D. B.

Composition of Glass suitable for Chemical Utensils. By R. Weber and E. Sauer (*Ber.*, **25**, 70—75).—The authors have determined the weight lost by flasks made of various glasses when water, sulphuric acid, hydrochloric acid, ammonia, sodium phosphate, and sodium carbonate are boiled in them for 3—5 hours.

The loss of weight is found to increase with the temperature, and is greater when the flask is heated over a bare flame than when heated in a water-bath.

In the experiments described, the flasks were heated under the same conditions on an iron plate covered with asbestos, with distilled water for five hours and with the other reagents for three hours. The authors give a table of the results obtained. They find that the best glass for chemical purposes contains silica, lime, and alkali in the proportion 8 : 1 : 1·5. They confirm the observations of other investigators, that the glass is attacked to a greater extent by water than by acids, and to a much greater extent by alkalis.

E. C. R.

Examination of Glass for Chemical Purposes. By F. Mylius and F. Foerster (*Ber.*, **25**, 97—99).—The authors have examined flasks made of 22 kinds of glass, and find that the most suitable glass contains silica, lime, and alkali in the proportion 7·2 : 1 : 1·1 (Weber and Sauer obtained the proportion 8 : 1 : 1·5; see preceding abstract). The experiments were carried out as follows:—The flask, after three days' treatment with water, was allowed to remain for three days with water at 20°, and the loss determined. It was then treated with water at 80°, and the loss again determined. From the similarity in composition of the glasses found to be most suitable for chemical purposes by the authors and by Weber and Sauer, the authors conclude that the determination of the action of water alone on glass is a criterion of its quality. E. C. R.

Green Chromic Sulphate. By A. Recoura (*Compt. rend.*, **113**, 857—860).—In presence of excess of sulphuric acid, a green chromium hydrogen sulphate is formed. A green modification of the normal sulphate is, however, obtained by reducing chromic anhydride with alcohol and sulphuric acid in presence of a quantity of water insufficient to dissolve the anhydride. 50 grams of chromic anhydride is mixed with 13 grams of water, and a mixture of 40 c.c. of concentrated sulphuric acid and 35 c.c. of alcohol of 95° is added drop by drop, care being taken that the temperature does not exceed 30°. The product is triturated with glacial acetic acid to remove organic matter, and then washed with anhydrous ether until all acid is removed. A pale-green chromium sulphate of the composition $Cr_2(SO_4)_3 + 11H_2O$ is thus obtained. It is extremely hygroscopic and deliquescent, rapidly forming a deep-green liquid when exposed to the atmosphere. It differs from the ordinary sulphate in that it gives no precipitate with lead or barium salts until after about half an hour. Precipitation is accelerated by heating, but is not complete until ebullition has been prolonged for several hours. If the solution has been prepared for some time, it gives an immediate precipitate in consequence of a partial spontaneous change into the violet modification. It is already well known that the green solution obtained by heating a solution of the violet chromium sulphate is only partially decomposed by barium chloride.

The green salt obtained by Étard by heating the crystallised violet sulphate at 100° has the composition $Cr_2(SO_4)_3 + 6H_2O$, but dissolves very slowly in water. If the violet sulphate is only heated at 90°, the residue has the composition $Cr_2(SO_4)_3 + 8H_2O$, dissolves readily in water, and seems to be identical with the green salt obtained in the manner described above. C. H. B.

Isomeric Forms of Chromic Sulphate. By A. Recoura (*Compt. rend.*, **113**, 1037—1040).—The green chromic sulphate which is prepared from the hydrated violet sulphate (preceding abstract) forms an aqueous solution which is quite distinct from the green solution obtained by heating that of the violet sulphate, and previously shown to contain a basic sulphate, $2CrO_3,5SO_3$ (Abstr., 1891, 1430). The new substance is not precipitated by barium

chloride or lead nitrate, but is thrown down by alkalis as a hydroxide, $Cr_2O(OH)_4$, which is shown by calorimetric measurements to be identical with that obtainable from chromium oxytetrachloride, Cr_2OCl_4. The solution changes spontaneously into that of the violet sulphate when kept, and may be transformed into that of the above-mentioned basic sulphate by adding in succession soda (2 mols.) equivalent to one-third of the acid present, and sulphuric acid (1 mol.).

Jn. W.

α-Orthostannic Acid. By G. Neumann (*Monatsh.*, **12**, 515—523; compare Löwenthal, *J. pr. Chem.* **77**, 324).—When a 5 per cent. solution of stannic chloride (2 parts) is mixed with a saturated solution of ammonium sulphate (1 part), a white precipitate is obtained, which, after washing and long-continued exposure to the air, gives, on analysis, numbers corresponding with the formula $Sn(OH)_4$. Saturated solutions of potassium and sodium sulphates may be substituted for the ammonium sulphate with production of the same substance; and it appears that the presence of hydrogen sulphide in the solution in no way alters the composition of the product. α-Orthostannic acid is readily soluble in hydrochloric acid, and may therefore be regarded as an isomeride of the hydrate of metastannic acid obtained by Fremy. It is, perhaps, identical with the acid obtained by Fremy and Weber, to which those authors ascribed the composition $3SnO_2,7H_2O$.

G. T. M.

Preparation of Pure Zirconium Chloride from Zircons. By F. P. Venable (*Chem. News*, **64**, 315—316).—The author has considerably modified Linnemann's method. The zircon is pulverised roughly in an iron mortar, and then ground in an agate mortar until the powder will pass through a 100-mesh sieve; the powder is boiled repeatedly with strong hydrochloric acid and washed with water. The fusion is conducted in a nickel crucible; 400 grams of sodium hydroxide are first fused, then 20 grams of dry sodium fluoride are added, and when the mass is highly heated, the 100 grams of zircon powder is dropped in; any boiling over of the mass is prevented by the temporary removal of the flame. When the action ceases, the molten mass is poured on to a sheet of nickel, and as soon as it solidifies is plunged into water; the sodium silicate and a negligible amount of the zirconate pass into solution, but the bulk of the latter remains behind, and is dissolved in hydrochloric acid, being then subjected to repeated evaporation to dryness and treatment with hydrochloric acid, to remove silica and hydrofluoric acid; the zirconium being ultimately precipitated as hydroxide by means of ammonia. The hydroxide, after thoroughly washing by decantation, is dissolved in the smallest possible quantity of strong hydrochloric acid, the solution evaporated to dryness, and the zirconium chloride obtained washed in a funnel with a mixture of strong hydrochloric acid with four parts of alcohol; any zirconium chloride passing into solution can be recovered. The white mass in the funnel is then repeatedly crystallised from strong hydrochloric acid, the zirconium oxychloride being obtained in well-formed crystals of glistening whiteness.

The author used North Carolina zircons, and found they contained

sodium, potassium, magnesium, calcium, aluminium, iron, lead, tin, uranium, erbium, silicon, and zirconium, the mean percentage of $Fe_2O_3 = 3{\cdot}29$, of $ZiO_2 = 62{\cdot}83$, of $SiO_2 = 33{\cdot}98$. Linnemann found 16 elements in his zircons, and does not mention tin as one.

D. A. L.

Solution of Antimonious Chloride in Saturated Solutions of Sodium Chloride. By H. Causse (*Compt. rend.*, **113**, 1042—1045).—When excess of antimonious oxide is added to cold hydrochloric acid, a state of equilibrium is established after a time between the oxide, the acid, the water, and the oxychloride resulting from the interaction of the water and the chloride. The amount of chloride formed increases with the strength of the acid, but the amount of the latter left uncombined is constant for all solutions containing more than 15 per cent. of hydrogen chloride. If the acid is saturated with sodium chloride, the curve representing the ratio of uncombined to total acid is not altered in character, but is brought nearer the abscissa, the proportion of free acid being less in every case; on the other hand, the amount of oxide dissolved is practically constant. A considerable amount of the acid in the solution thus saturated with sodium chloride may be neutralised with sodium carbonate without precipitating the antimony, and actual titration shows that the amount of alkali added is exactly equivalent to the free acid, so that antimonious chloride can remain dissolved in an aqueous solution of sodium chloride. Jn. W.

Antimony Thiophosphate. By E. Glatzel (*Ber.*, **24**, 3886—3888).—*Antimony thiophosphate*, $SbPS_4$, is obtained by the action of antimony trichloride or antimony trisulphide on phosphorus pentasulphide. Finely powdered phosphorus pentasulphide (40 grams) and antimony trichloride (80 grams) are mixed together by shaking in a retort and warmed for one hour on the sand-bath with the neck of the retort pointing upwards; when the reaction is ended, the phosphorus thiochloride and excess of antimony trichloride are distilled off. The antimony thiophosphate which remains in the retort is bright-yellow; it melts when the temperature is raised, and solidifies on cooling in radiating, fibrous crystals of brilliant, silky lustre; when ground up, it yields a straw-coloured felted mass which smells of hydrogen sulphide, is insoluble in water, alcohol, ether, carbon bisulphide, hydrochloric acid, dilute sulphuric acid, benzene, and acetic acid, but is decomposed when boiled with strong nitric acid, aqua regia, strong sulphuric acid, and potassium or sodium hydroxides, and burns with a pale flame when heated in the air. When heated at its melting point for some time, decomposition takes place, a part of the phosphorus pentasulphide distils off, and a ruby-red, amorphous mass is left in the retort.

The preparation from antimony trisulphide is carried out in the same way as described above from the trichloride.

The author is preparing other thiophosphates. E. C. R.

Bismuthic Acid. By G. André (*Compt. rend.*, **113**, 860—862).—20 grams of bismuth bromide and 40 grams of potassium brom-

ide are dissolved in 60 grams of water and mixed with excess of bromine. The solution is then poured drop by drop into an almost boiling solution of 100 grams of potassium hydroxide in 150 grams of water, the alkali remaining in excess at the end of the reaction. A very dense, red-brown precipitate forms immediately. This is washed repeatedly with boiling water by decantation, and after a long time part of the product forms a brown emulsion with the water, whilst a red-brown compound remains at the bottom of the vessel. The emulsion is decanted off, and can be precipitated by addition of a few drops of nitric acid. The non-emulsified product was washed with hot water until no longer alkaline, and one portion was washed for several days longer. Both portions, when dried at 100°, had the composition $4KBiO_3,3HBiO_3$. The same product is obtained from bismuth chloride. It dissolves easily in hydrochloric acid, with evolution of chlorine, but is soluble only with difficulty in warm nitric acid. When heated, it becomes pale-yellow, loses oxygen, then becomes brown, melts, and, on cooling, is pale-yellow.

Prolonged washing with boiling water yields a product which, after being dried at 100°, has the composition $KBiO_3,HBiO_3$.

All these products when treated with warm, dilute nitric acid, lose the whole of their potassium and yield brick-red bismuthic acid, $HBiO_3$. Very often the residue dried at 100° has the composition $HBiO_3,Bi_2O_5$. C. H. B.

Mineralogical Chemistry.

Determination of the Melting Points of Minerals. By J. Joly (*Chem. News*, **65**, 1—3, 16—18, 30—32, and 41—44).—Up to the present, no serious attempt has been made to measure accurately the melting points of minerals. The scale of fusibility of Van Kobell constitutes a comparative method, but is full of errors even as a means of identification. Whether a splinter of a mineral will melt in the flame of the blowpipe depends as much on the shape, conductivity, and dimensions of the splinter as on its melting point. In order to avoid these sources of error and to obtain an accurate measure of the melting points of minerals, the author has designed an instrument which he terms a "meldometer"; it is constructed as follows:—A ribbon of pure platinum, having a width of about 1·2 mm., is stretched between forceps, furnished each with a binding screw, and insulated from each other so that on connecting the binding screws with a battery a current can be passed through the ribbon. Upon the surface of this ribbon the substance to be examined is placed. It is necessary first to reduce the mineral to a fine powder in an agate mortar, and finally grind it with a little water in the form of a fine fluent paste; a speck of this is spread over a small area of the ribbon. The best condition for observing melting is when a

few particles are thinly spread here and there upon the platinum. A quantity invisible to the unassisted eye may be dealt with, for in all cases the phenomena of melting are observed through a microscope. The microscope having been brought to bear upon the thin coating of the powdered mineral upon the platinum, a current of gradually increasing intensity is passed through the ribbon until the mineral melts or volatilises. In this process the mineral often exhibits very characteristic phenomena, so that a substance may be identified in this way by comparing its behaviour with that of accredited specimens of the material in question. By this method, also, sublimates may be readily obtained, even from substances which treated in the blowpipe would appear to afford none. A circular cover-glass, not too thin, grasped in a forceps, is held horizontally above the platinum ribbon, as the temperature is being raised. If the sublimate is one which oxidises, we obtain the oxidised sublimate alone, or the unoxidised sublimate bordered by the oxide, according as we hold the glass further or nearer to the ribbon.

In order to measure the exact melting points of the substances dealt with, the author, after trying different methods for the estimation of the temperature, has adopted one which depends on the thermal expansion of the ribbon. The increase in length of the ribbon is determined when a salt of known high melting point is seen to melt upon its surface, and again when two or more other substances differing from each other as much as possible in melting point are melting. With several such points, a curve can be constructed for the extension of the ribbon with temperature, from which the temperature of melting of any unknown substance can be at once ascertained, when the extension of the ribbon at the time of melting is known. Full details of the method of measuring the extension of the ribbon are given in the paper. H. C.

Natural Classification of Minerals. By T. Sterry Hunt (*Systematic Mineralogy*, New York, 1891).—In a volume of 391 pages, the author describes a method of classification of minerals designed with the object of reconciling the natural history method and the chemical method, between which the antagonism in former years was the subject of much debate. His primary division, based on chemical grounds, is into four classes: (1) The non-oxidised metallic minerals, (2) the haloïd minerals, (3) the oxidised minerals, and (4) the carbonaceous combustibles. The further subdivisions are chemical and physical, use being made of the periodic law, and of the law of polymerism. By dividing the calculated value of the chemical unit for each species by its specific gravity, the author obtains a constant which he terms the reciprocal of the coefficient of condensation, and this figure furnishes a means of classification with which hardness and other physical properties coincide to a remarkable degree.

B. H. B.

Paramelaconite and Footeïte. By G. A. Koenig (*Zeit. Kryst. Min.*, **19**, 597—603).—At the Copper Queen Mine, at Bisby, in

Arizona, Mr. A. E. Foote found two interesting specimens, which probably once were portions of the same piece. The specimens consist of black crystals with an adamantine lustre planted on a matrix composed of acicular, indigo-blue crystals. The black crystals, termed *paramelaconite* by the author, are of the tetragonal system, closely resembling the black anatase of Brazil. The colour of the crystal faces is violet-black, whilst that of the fractured surface is raven-black. The hardness is 5, and the sp. gr. 5·833. Analysis yielded 100·68 per cent. of CuO, and 0·64 per cent. of Fe_2O_3, or, if the excess is taken to be oxygen, the material analysed consisted of—

CuO.	Cu_2O.	Fe_2O_3.	Total.
87·66	11·70	0·64	100·00

This represents, therefore, an undoubted case of dimorphism of black cupric oxide, a mineral hitherto found to crystallise in the asymmetrical system. On the conclusion of the investigation, the author discovered another specimen of this mineral, described as melaconite or tenorite from South Arizona, in the collection of the University of Pennsylvania.

The small, acicular crystals, termed *footeïte* by the author, are of the monosymmetrical system, and gave on analysis results corresponding with the formula $8Cu(HO)_2,CuCl_2 + 4H_2O$. The mineral approaching most closely to this composition is Church's blue thallingite. B. H. B.

Samarskite from Colorado. By W. F. Hillebrand (*Zeit. Kryst. Min.*, **19**, 638—640; from *Proc. Colorado Sci. Soc.*, **3**, 38—47).—The mineral examined was obtained from the Devil's Head Mountain, Douglas Co., Colorado. It occurs in small fragments without crystalline form. It has a hardness of 5·5 to 6, a sp. gr. of 6·18, a pitch-black colour, a dirty-brown streak, and a conchoidal fracture. A second specimen had a salmon-coloured streak and a sp. gr. of 6·12, whilst a third specimen was so highly altered that the original colour and lustre could no longer be observed. Analyses of the three specimens are given by the author.

With this mineral, there occurs another, which appears, according to analyses given by the author, to consist of a mixture of a mineral resembling cyrtolite and of a phosphate. B. H. B.

Formation of Melilite during the Burning of Portland Cement. By G. Bodländer (*Jahrb. f. Min.*, 1892, i, Mem. 53—56).—On emptying the chamber of an annular kiln at the Ascania Cement Works, at Nienburg, there was found, with the compact cement clinkers, a porous mass, about the size of the fist, which was filled with tabular, tetragonal crystals about 3 mm. in diameter and 1·5 mm. in height. The crystal planes are of light-brown colour, and the fractured surfaces are greyish-yellow. On analysis, it was found that this mineral was melilite. It appears to have been formed by the action of the acid fire-bricks, with which the kiln was lined, on the basic mass of cement. B. H. B.

Relation between Minerals of the Heulandite and Desmine Groups. By F. Rinne (*Jahrb. f. Min.*, 1892, i, Mem. 12—44).—The heulandite group consists of the minerals heulandite, brewsterite, and epistilbite, and the desmine group consists of desmine, harmatome, and phillipsite. From a consideration of the geometrical relations of the crystals of these minerals, it is shown that heulandite, brewsterite, and epistilbite may, in view of their external form, be regarded as one group of isomorphous minerals, bearing a relation to the group of isomorphous minerals composed of harmatome, phillipsite, and desmine. The mean axial ratios of the minerals of these groups are :—

Heulandite group.. $a:c:b = 1:0{\cdot}8611:1{\cdot}7520$; $\beta = 56° 2'$
Desmine group.... $a:c:b = 1:0{\cdot}8479:1{\cdot}3811$; $\beta = 53\ 52'$

With regard to the composition of these minerals, W. Fresenius has shown that harmatome, phillipsite, and desmine are members of a series of silicate mixtures. In the case of the heulandite group, the author proposes the following formulæ, based on analyses made by Jannasch :—

Heulandite ..... $RAl_2Si_6O_{16} + 6H_2O$.
Epistilbite ..... } $RAl_2Si_6O_{16} + 5\frac{1}{2}H_2O$.
Brewsterite ..... }

In heulandite R represents Ca, Sr, Na_2, K_2, Li; in epistilbite, Ca, Na_2, K_2, Li_2; and in brewsterite, Si, Ba, Ca, Na_2, K_2.

Interesting relations are also pointed out in the physical properties of these minerals. The individuality of the six minerals is rendered evident, and they may well be classed together as one great natural group of zeolites. B. H. B.

Formula of Vesuvian Meionite. By A. Kenngott (*Jahrb. f. Min.*, 1892, i, Mem. 49—53).—With a view to find a formula for meionite which would be in accord with Tschermak's theory, that the scapolite series consists of mixtures of a lime-alumina silicate and a soda-alumina silicate, the author has recalculated the published analyses of meionite from Vesuvius, and arrives at the formula $Ca_7Al_{10}O_{22},Si_{11}O_{22}$ as the most probable. It is that of a basic silicate in which the ratio of the oxygen in the lime and alumina to that in the silica is as 1 is to 1, and the ratio of the calcium, aluminium, and silicon atoms to the oxygen atoms is as 7 is to 11. B. H. B.

Rumpfite, a New Mineral. By G. Firtsch (*Jahrb. f. Min.*, 1892, i, Ref. 31—32; from *Sitzungsber. Wien. Akad.*, **99**, 1—5).—In fissures in the pinolite in the recently-discovered dolomite mass near St. Michael, in Upper Styria, there is found, with talc, a greenish-white mineral, with a perfect basal cleavage, a white streak, a hardness of 1·5, and a sp. gr. of 2·675. The mineral is optically uniaxial, and probably belongs to the hexagonal system, unless it is monoclinic, with a very small axial angle. Analysis yielded the following results :—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
30·75	41·66	1·61	0·89	12·09	13·12	100·12

The formula is, consequently, $H_{28}Mg_7Al_{16}Si_{10}O_{65}$. The new mineral re sembles most closely the chlorites, from which, however, it differs in chemical composition. B. H. B.

Meteorites of Turgaisk. By E. D. Kislakowsky (*Jahrb. f. Min.*, 1892, i, Ref. 51—52; from *Bull. soc. imp. des naturalistes de Moscou*, **4**, 187—199).—Two pieces have been found, weighing $32\frac{1}{2}$ and 16 kilograms respectively. Their sp. gr. was 6·6. Analysis showed them to consist of a portion amounting to 78·51 per cent. soluble in nitric acid, and containing :—

Fe.	Ni.	Co.	P.	Cu.	Total.
73·00	3·85	1·63	0·02	trace	78·50

whilst the residue contained :—

Fe.	Ni.	P.	Al_2O_3.	CaO.	MgO.	SiO_2.	Total.
2·99	1·15	0·30	2·86	1·56	4·77	7·67	21·30

The meteorite was calculated to consist of 3·85 per cent. of schreibersite, 9·88 of olivine, 8·06 of anorthite, and 78·25 of meteoric iron. The meteoric iron contained 93·10 per cent. of iron, 4·82 of nickel, and 2·08 of cobalt. The proportion of cobalt is unusually high, whilst that of the nickel and cobalt together is remarkably low for an octahedral iron. B. H. B.

Mineral Springs of Edepsos. By A. K. Dambergis (*Ber.*, **25** 99—107).—The springs of Edepsos are scattered over an area measuring 600 metres from east to west and 500 metres from north to south. Their number is about 60, but if all the small cracks from which water flows are counted, then they number above 100. They lie at an altitude varying from 48·78 to 5·60 metres above the sea level. The temperature of the water varies from 28° to 78°, and the highest springs have usually the lowest temperature. The volume of water from all the springs amounts to 8640 cubic metres per 24 hours. The water bubbles out clear, but on exposure to air soon deposits a precipitate; it tastes very salt and somewhat bitter. The steam which comes out with the water smells slightly of hydrogen sulphide, but the water itself is odourless. The specific gravity varies from 1·0168 to 1·0194, compared with distilled water at 25°. Nearly all the springs evolve a large volume of gas, which consists almost entirely of carbonic anhydride mixed with small quantities of oxygen and nitrogen, and sometimes a very small quantity of hydrogen sulphide. The deposit from the water varies in colour from white to reddish-brown; the white deposit consists of calcium carbonate with small quantities of magnesium carbonate, calcium sulphate and phosphate, alumina, and ferric oxide. Some of the springs give a red deposit, which consists of almost pure ferric oxide. In the neighbourhood of the springs are several cracks from which hot gas is

evolved. This gas varies in temperature from 46° to 62°, and consists of air, carbonic anhydride, and steam. The amount of solid in the water per 100 c.c. varies from 22·9582 grams to 33·5840 grams. A table is given containing a complete analysis of several of the waters.

E. C. R.

Waters of the North Sea on the Coasts of Holland. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **10**, 91—99).—In 1889, a series of samples of water, taken at 50—60 m. from the coast near Scheveningen, were examined by Koppeschaar. When the lock of the "Ververschingskanaal" was closed, the minimum amount of sodium chloride found was 17·96 grams per litre, and the maximum, 29·64 grams. These numbers correspond with the specific gravities of 1·0146 and 1·0241 at 15°.

A commission, continuing these researches, in 1890 examined 268 surface samples. The specific gravity varied from 1·0103 to 1·0241. The variations were due to fresh water from the "Nieuwe Waterweg." They were generally gradual, but instances are given of sudden variations. With increasing depth, these variations became less considerable and not so well defined. In 20 samples, at a depth of 1 to 2·5 m., the density varied from 1·0131 to 1·0233; 105 samples from the bottom, at 2·5—5 m., showed a variation from 1·0162 to 1·0239; 18 samples taken from the bottom, at 7·2—9·4 m., gave 1·0211—1·0245. With 88 samples collected when the lock gates were closed, the proportion of ammonia varied from 0 to 0·4 milligram per litre. In the greater number of cases, the quantitity of ammonia did not reach 0·1 milligram per litre.

82 analyses gave the maximum and minimum amounts of permanganate required for oxidation of the organic matter in boiling alkaline solution as 7·2 and 2·0 milligrams per litre. There is a distinct relation between the specific gravities and the amounts of potassium permanganate required; the smaller densities correspond with the higher values for permanganate.

The amounts of suspended matter varied between wide limits. Among 139 samples not contaminated with the waters of the canal, 63 per cent. gave below 30 milligrams per litre of sediment, which consisted, in great part, of organic matter. When the sediment exceeded 60 milligrams per litre, the loss by calcination became very constant at about 20 per cent.

An analysis by Van Bemmelen of the whole of the residues collected and air-dried gave:—4·25 per cent. of water, $\pm$11 per cent. of organic matter, 19·6 per cent. of calcium carbonate, 8 per cent. of coarse sand, 23 per cent. of fine sand and clay deposited from the water, and 33·5 per cent. of true clay, remaining suspended in pure water for 24 hours. The composition of the North Sea sediment is thus similar to that of the Ij, Zuider Zee, and Dollard.

The organic matters are chiefly composed of fragments of marine animals and plants.

W. T.

Organic Chemistry.

Ammonio-Copper Ammonium Cyanide. By E. Fleurent (*Compt. rend.*, **113**, 1045—1047).—When copper hydroxide is dissolved in a freshly made boiling solution of ammonium cyanide, two distinct substances, which crystallise in large, violet or brown needles, separate on cooling. The author has not succeeded in determining the nature or conditions of formation of these compounds.

A stable ammonio-copper ammonium cyanide,

$$Cu_2(CN)_2,NH_4CN,3NH_3,$$

however, may be prepared by treating a solution of cupric chloride (15 grams) with excess of ammonia, adding ammonium chloride (3 grams) and potassium cyanide (22 grams), and heating the resulting solution (200 c.c.) in sealed tubes at 125—130° for three hours. The colourless liquid thus obtained, which loses ammonia and deposits colourless crystals on exposure to the air, is treated with acetic acid until a precipitate begins to form, after the removal of which the double cyanide separates in colourless, hexagonal plates. It is insoluble in cold water, and only sparingly soluble in hot water, but freely in ammonia, in which it forms a colourless solution which turns blue on exposure to the air. When heated above 200°, it loses ammonia and ammonium cyanide, and is converted into cuprous cyanide. When treated with dilute nitric or sulphuric acid, it is converted into cupric and hydrogen cyanides.

The author has obtained other compounds by varying the conditions, and has also prepared analogous bromides and iodides, which he is at present studying. Jn. W.

Dibromopropylene. By R. Lespieau (*Bull. Soc. Chim.* [3], **6**, 420—421).—The dibromopropylene, $CHBr{:}CH{\cdot}CH_2Br$ (termed by the author epidibromhydrin) has been prepared by the method employed by Friedel for the corresponding chlorine compound. Symmetrical dibromhydrin is treated with phosphorus pentoxide and distilled under reduced pressure. The product separates into two main portions: one of these is tribromhydrin boiling at 219°; the other boils with decomposition at 155°. The latter passes over at about 91° under 105 mm. pressure. It is colourless, but becomes yellowish-red in the light. Its formula is $C_3H_4Br_2$; the cryoscopic method with benzene gives its molecular weight as 198·27 as against the calculated value 200. Its density at 0° is 2·12. It takes up two atoms of bromine less energetically than its isomeride,

$$CH_2{:}CBr{\cdot}CH_2Br.$$

The product obtained does not solidify in a mixture of ice and salt, whereas its isomeride solidifies at about 0°.

Sodium ethoxide reacts on this compound at 0°, giving the ether $CHBr{:}CH{\cdot}CH_2{\cdot}OEt$. It is an oil insoluble in water, boiling at 145—146°, and of sp. gr. 1·47. Its molecular weight is found by

the cryoscopic method to be 160·58. Traces of propargyl methyl ether are formed at the same time, and this substance is the product when the oil is treated with sodium. W. T.

Formation of Acetylene from Bromoform. By P. Cazeneuve (*Compt. rend.*, **113**, 1054—1055).—Acetylene has been synthesised in various ways from chloroform and iodoform, but not hitherto from bromoform. When bromoform (10 grams) is warmed with dry powdered silver (50 grams), a reaction occurs which is so violent as to raise the mass to incandescence, and acetylene is evolved in nearly theoretical quantity. Powdered zinc may be substituted for the silver, but the action must then be started by allowing a few drops of ammoniacal cuprous chloride to trickle down the sides of the containing vessel. If a steady stream of the gas is required, it is best to use the copper-zinc couple, for which purpose the bromoform (20 grams) is treated with powdered zinc (80 grams), and 2 per cent. aqueous cupric chloride. Chloroform does not yield acetylene under these methods of treatment, except, perhaps, a trace with the copper-zinc couple. Jn. W.

Preparation of Cuprous Acetylide. By M. Kuntzmann (*Bull. Soc. Chim.* [3], **6**, 422).—The author prepares this compound by the action of acetylene on copper in presence of ammonia, whereby (1) the intermediate formation of ammoniacal cuprous chloride is obviated, and (2) it is not necessary to wash with ammonia as in the ordinary method of preparation. The gases containing acetylene are aspirated through a Woulffe's bottle containing ammonia solution, and thence through a cylinder containing copper turnings and ammonia. The red compound forms on the turnings and remains in suspension in the liquid, which itself becomes blue. In connection with a Jungfleisch apparatus for burning gas, 20—25 grams of the red compound have been obtained per hour, using 125 grams of commercial ammonia. W. T.

Action of Potassium and Sodium Sulphides on Chloroform. By L. Delmont (*J. Pharm.* [5], **24**, 425—429).—The action of alkaline sulphides on chloroform leads first to the formation of *thioformic acid*, CH_2S_2, now first obtained, next, to the production of intermediate chlorine compounds from which the thioxanthates can be regularly obtained, and, lastly, to the formation of alcoholates of the alkaline bisulphate. J. T.

Disodium Glycol. By De Forcrand (*Compt. rend.*, **113**, 1048—1051).—Disodium glycol cannot be obtained by the direct action of sodium on monosodium glycol, as this substance is solid, and cannot be heated in contact with sodium without decomposition. It may, however, be prepared by treating glycol with saturated aqueous soda (2 or 3 mols.), and evaporating the solution over phosphoric anhydride in the cold, when, after several days, brilliant plates of the hydrated compound, $C_2H_4Na_2O_2 + 10H_2O$, crystallise out. The anhydrous compound may be obtained as a white, amorphous,

porous mass by heating the hydrated compound in a current of hydrogen at 130°. The yield is only 8 to 10 per cent. Another method, which is better adapted for calorimetric study, and which gives practically the theoretical yield, consists in treating glycol with sodium ethoxide (2 mols.) in alcoholic solution. The glycol dissolves with evolution of heat, and the solution is boiled in a reflux apparatus for two or three hours, after which the alcohol is distilled off in a current of hydrogen, and the residue heated at 135° until it ceases to lose weight. The product thus obtained appears, however, to contain a little unchanged glycol.

The heat of solution of disodium glycol in water (1 gram mol. in 6 litres at 10°) is +21·49 Cal.; the heat of combination of glycol (1 gram mol. in 2 litres of water) with 1 eq. of sodium hydroxide (1 gram. mol. in 2 litres of water) is +0·28 Cal.; and that of monosodium glycol with sodium hydroxide under the same conditions is +0·08 Cal. From these data, and the assumption that the heat of fusion of glycol is the same as that of glycerol, −3·9 Cal., it is calculated that the first equivalent of sodium in displacing the hydrogen from glycol liberates +35·10 Cal., whilst the second liberates +27·68 Cal. There is thus a difference of +7·42 Cal. in favour of the first equivalent, which is also the case with glycerol and erythritol, for which the corresponding differences are +9·57 Cal. and +7·00 Cal. It is to be remarked also that the heat disengaged by the first equivalent of sodium in each of these three cases (+35·10, +39·99, +37·14 Cal.) is greater than that disengaged by the action of sodium on water (+31·87 Cal.; the water calculated as solid), while that disengaged by the action of the second equivalent (+27·68, +30·42, +31·16 Cal.) is distinctly less. Jn. W.

Compounds of Sorbitol and Perseïtol with Molybdic Acid. By D. Gernez (*Compt. rend.*, **113**, 1031—1033).—The rotatory power of sorbitol, like that of mannitol (Abstr., 1891, 1443), is affected by the presence of certain acid molybdates. When, for instance, sodium hydrogen or ammonium hydrogen molybdate (1/168 mol.) is added to an aqueous solution of sorbitol (1 mol.), the (negative) rotatory power is halved; it is destroyed, moreover, by the addition of double this amount, and, by still further additions, is reversed. The positive increase does not, however, continue indefinitely, as with either of the above salts a maximum is reached when 0·28 mol. has been added, the rotatory power at this point being numerically 20 times that of the original solution. This proportion would seem to indicate the presence of a compound of 1 mol. of sorbitol with 2 mols. of molybdic acid, but since the neutral molybdates are entirely inert towards polarised light, and the action of the acid salts may, therefore, be supposed to be due to the excess of acid, it is more likely that the compound present in the solution consists of 8 mols. of sorbitol with 9 mols. of the acid. Similar results are stated to have been obtained with perseïtol. Jn. W.

Preparation of Raffinose from Molasses. By J. W. Gunning (*Chem. Centr.*, 1891, ii, 798; from *Bull. assoc. belg. des chimistes*, 1891,

326).—The author uses the following method for the separation of raffinose from molasses :—The amount of a saturated solution of alum which is necessary to neutralise the molasses is determined in about 10 grams. A quantity of 1—5 kilos. of molasses is employed, water is added, together with the requisite quantity of alum solution, and then sufficient methyl alcohol to make it 60 per cent. The liquid is now filtered, and lead acetate added until no further precipitate forms. The precipitate is filtered off, and the solution neutralised with barium hydroxide and again filtered. In 50 c.c. of this solution, the amounts of raffinose and saccharose are estimated. From the remainder of the solution, the methyl alcohol is distilled, and the solution concentrated to a syrup. Whilst still warm, it is poured into a hot solution (1 : 1) of barium hydroxide in the proportion of 1 part of barium to 1 of sugar; the last portions are transferred by means of 50—100 c.c. of hot water. The mixture is boiled until a thick precipitate forms, when the latter is pressed from the solution. The solution is now concentrated to half the volume, and barium hydroxide solution added in the proportion of 2 mols. to 1 mol. of raffinose. Sufficient methyl alcohol is added to represent 75 per cent., and the liquid shaken thoroughly, when the barium raffinosate separates in agglomerations, which may easily be collected. It is washed with cold 75 per cent. methyl alcohol, dissolved in water, the barium precipitated by carbonic anhydride, the solution boiled, filtered, concentrated under diminished pressure to a syrup, and allowed to crystallise for two or three days. The crystalline mass is now washed with 60 per cent. methyl alcohol until all the saccharose is separated and then pressed. The raffinose is again dissolved in about seven times its weight of methyl alcohol, a little blood charcoal added, if necessary, and again allowed to crystallise. By this means, from 20—30 per. cent. of the raffinose present in the molasses is obtained. J. W. L.

Formaldehyde. By G. Lösekann (*Chem. Zeit.*, **14**, 1408—1409).—If paraformaldehyde be dissolved in hot water and the solution allowed to cool, or if it be rubbed with a little alcohol twice or thrice, the alcohol pressed out, and the residue treated similarly with ether, and then dried in a current of dry air, a white powder is obtained, which dissolves readily in hot water, and which is almost completely deposited again on cooling the solution. This substance was found to contain 88·2 per cent. of formaldehyde, as determined by Legler's method. After passing dry air over it for 40 minutes, 91·5 per cent. of formaldehyde was found. It was completely soluble in ammonia. After keeping in a stoppered tube for some time, 92·7 per cent. of formaldehyde was found. Trioxymethylene did not react like the paraldehyde, and the author concludes that trioxymethylene is, in reality, hexaoxymethylene, whilst paraldehyde is hexaoxymethylene hydrate. By passing hydrogen chloride into aqueous formaldehyde, a series of hydrochlorides were obtained, the first formed being $2CH_2O,HCl$, whilst $3CH_2O,2HCl$, $6CH_2O,5HCl$, and CH_2O,HCl were also obtained. J. W. L.

Action of Sulphurous Anhydride on Crotonaldehyde. By G. Haubner (*Monatsh.*, **12**, 541—555).—The author has extended the work of Ludwig (Abstr., 1889, 121) and Haymann (*ibid.*, 487) to crotonaldehyde, and finds that it also combines readily with sulphurous anhydride when that gas is led into its aqueous solution, kept cold with ice. The product is *hydroxybutanedisulphonic acid*, of which the barium salt, $C_4H_8S_2O_7Ba + 3H_2O$, forms an amorphous, white mass. The aqueous solution of this acid, on concentration, loses sulphurous acid and is converted into *butaldehydesulphonic acid*, which gives a gummy barium salt, $(C_4H_7SO_4)_2Ba + H_2O$. On oxidation with chlorine, hydroxybutanedisulphonic acid is converted into *β-sulphobutyric acid*, $SO_3H{\cdot}CHMe{\cdot}CH_2{\cdot}COOH$, the barium salt of which is very soluble in water, but almost insoluble in alcohol. The last-named acid gives acetic acid on fusion with potash, and consequently the sulpho-group is in the *β*-position, the compound having the constitution indicated above.

Barium butaldoximesulphonate is formed when hydroxylamine and baryta are heated with butaldehydesulphonic acid for four hours. On the addition of alcohol to its aqueous solution, it forms an amorphous precipitate; it has the constitution

$$(NOH{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}SO_3)_2Ba,$$

and, on reduction with sodium amalgam and subsequent distillation with lime in an atmosphere of hydrogen, gives a mixture of crotylamine, $CHMe{:}CH{\cdot}CH_2{\cdot}NH_2$, and butylamine.

On reduction of butaldehydesulphonic acid with sodium amalgam, the *sodium salt* of hydroxybutane-β-sulphonic acid, $C_4H_9SO_4Na$, is obtained. It is a hygroscopic, pale yellow salt, which, on distillation with lime, gives a mixture of crotyl alcohol and butyl alcohol.

G. T. M.

Action of Chlorine on some Ketones of the Fatty Series. By Démètre-Vladesco (*Bull. Soc. Chim.*, **6**, 395—415).—The action of chlorine on the four ketones—methyl ethyl ketone, methyl propyl ketone, propione, and butyrone—has been studied by the author, and a part of his results appear in this paper.

Methyl ethyl ketone and methyl propyl ketone are found among the products of distillation of wood, and have been prepared from light oils obtained in the rectification of methyl alcohol. In order to extract them, the portion distilling between 85° and 140° is washed with distilled water. The residue, insoluble in water, is treated with sodium hydrogen sulphite, and the solid compound formed freed from a liquid not combining with the sulphite and distilled with sodium carbonate. The product is fractionated. That portion passing over from 99° to 100° has the formula $C_5H_{10}O$, and was proved to be methyl propyl ketone. The portion distilling between 70° and 143° is treated with distilled water. The part of the light oil dissolved is then separated with potassium carbonate; the product is treated with sodium hydrogen sulphite, and the ketone combining therewith is recovered and fractionated. The fraction passing over between 79° and 82° is methyl ethyl ketone. It has been identified by the preparation of its oxime, the corresponding secondary alcohol, and methyl ethyl chloracetole.

12 kilos. of light oils, obtained during the rectification of 20,000 litres of methyl alcohol, yielded 600 grams of pure methyl ethyl ketone.

A slow current of chlorine, dry and free from hydrochloric acid, was passed through 500 grams of methyl ethyl ketone, contained in a reflux apparatus and cooled by immersion in a freezing mixture. The hydrogen chloride formed during the operation was absorbed in distilled water in a tared flask. By weighing this flask at intervals, the progress of the reaction was ascertained. The experiment was stopped when the weight of hydrogen chloride disengaged equalled half the weight of the ketone used. The chlorination occupied three days. Fractional distillation yielded two main products. The one, passing over at 114—116°, when redistilled under a pressure of 365 mm., allowed the isolation of a liquid boiling at 115° at 755 mm., and having the composition C_4H_7ClO. Its vapour density, by V. Meyer's method in aniline, was found to be 3·8 as compared with 3·7, the theoretical value. The other, passing over at 164—166°, when similarly treated, gave the pure compound, boiling at 165° at 753 mm., and of the composition $C_4H_6Cl_2O$, this formula being confirmed by its density of 4·8. Both substances are liquids insoluble in water.

The chlorinated ketone, $CH_3{\cdot}CO{\cdot}CHCl{\cdot}CH_3$, was prepared by Conrad's method, and its properties were found to agree with those of the monochlorinated derivative of methyl ethyl ketone. The chloroketone, $CH_3{\cdot}CO{\cdot}CHCl{\cdot}CH_3$, was obtained as follows:—The sodium derivative of ethyl methylacetoacetate, dissolved in absolute alcohol, was acted on by the calculated quantity of dry chlorine, the sodium chloride filtered off and the chlorine derivative remaining freed from alcohol by evaporation on the water-bath. This substance,

$$COMe{\cdot}CMeCl{\cdot}COOEt,$$

was then heated for 6 hours with dilute hydrochloric acid at 170—180° in sealed tubes. The chloro-ketone thus obtained was then distilled off. Chlorethyl methyl ketone, $COMe{\cdot}CHClMe$, yields with zinc methyl a substance which readily combines with sodium hydrogen sulphite and distils between 85° and 100°. It is inferred that the substance synthesised is methyl isopropyl ketone, which boils at 95°, and from this it follows that the formula given above represents the constitution of the monochlorinated derivative of ethyl methyl ketone.

Constitution of the Compound $C_4H_6Cl_2O$.—There are six possible isomerides of this formula; among these, the two most probable are $COMe{\cdot}CCl_2Me$ and $CH_2Cl{\cdot}CO{\cdot}CHClMe$. By treatment with hydroxylamine, in presence of sodium acetate, the two chlorine atoms are replaced by the group NOH, this acting in the same manner as the oxygen atom. Hence the formula $CH_3{\cdot}CO{\cdot}CCl_2{\cdot}CH_3$ probably represents the constitution of the dichlorinated derivative obtained from methyl ethyl ketone. W. T.

Preparation of Fatty 1 : 2-Diketones. By H. v. Pechmann (*Ber.*, **24**, 3954—3956).—The following method of preparing diacetyl has been found to give the best results:—100 grams of ethyl methylacetoacetate is mixed in a narrow-mouthed bottle of 5 litres capacity

with 1·75 litres of water and 280 grams of 25 per cent. soda solution, and allowed to remain over night; 50 grams of 98 per cent. sodium nitrite are then added, the whole cooled in ice-water, and treated in small portions with 20 per cent. sulphuric acid, a rapid current of air being drawn through the liquid during the process to ensure the thorough admixture of the substances. As soon as tropæolin paper is coloured violet by the solution, the addition of sulphuric acid is stopped, the whole made alkaline with soda, and again slightly acidified with sulphuric acid. The product is divided into two portions, each of which is treated with soda until yellow, mixed with 150 grams of sodium carbonate crystals, and boiled until one half of the liquid has distilled over; the residue is neutralised with dilute sulphuric acid, diluted to 1·75 litres, mixed with 250 grams of concentrated sulphuric acid without cooling, and quickly distilled. The diacetyl passes over with the steam, the distillation being complete when the liquid gives no yellow coloration with soda. The first distillate also contains a certain amount of nitroso-ketone, which may be recovered by adding soda until it is yellow, then 50 grams of sodium carbonate crystals, distilling off the alcohol, adding sulphuric acid to the residue, and again distilling until no more diacetyl passes over.

All the distillates, which contain in addition to diacetyl some unaltered nitroso-ketone, are united and distilled with one-seventh their weight of concentrated sulphuric acid until no more diketone passes over, and the new distillates again distilled with addition of common salt; the process being repeated until the diacetyl separates from the aqueous solution as a light yellow oil, which is dried by fused calcium chloride, and distilled. The pure compound boils at 87—88°.

Acetylpropionyl can be obtained from ethyl ethylacetoacetate in an exactly similar manner; it boils, when pure, at 108°. H. G. C.

Configuration of Fatty Ketoximes. By A. Hantzsch (*Ber.*, **24**, 4018—4024).—Previous investigations have shown that aldoximes, and the oximes of symmetrical ketones, exist only in one form, which may be represented by the configuration $C_nH_{2n+1}\cdot C(N\cdot OH)\cdot R$; as the oximes of the lower asymmetrical ketones of the fatty series are liquids, the question whether they exist in two stereoisomeric modifications can only be settled indirectly by studying their chemical behaviour. This the author has attempted to do by treating the ketoximes with phosphorus pentachloride in ethereal solution, and then boiling the product with potash; in every case, the oxime behaved as if it were a mixture of two stereoisomeric forms, and yielded two amines and two fatty acids. The oxime of methyl ethyl ketone, for example, gives ethylamine and smaller quantities of methylamine, acetic acid, and a still smaller quantity of propionic acid; it may, therefore, be concluded that it is converted by phosphorus pentachloride and water successively into ethylacetamide and smaller quantities of methylpropionamide, that is to say (assuming an explanation of the reaction, given by the author with the aid of graphic formulæ, to be correct), that it consists of the stereoisomerides of the configurations

$Me\cdot\overset{\|}{C}\cdot Et$ and $Me\cdot\overset{\|}{C}\cdot Et$ respectively, the former being present in
$N\cdot OH$ $OH\cdot N$
the larger proportion.

The oxime of methyl propyl ketone, when treated in like manner, gives propylamine and a small quantity of methylamine, acetic acid, and a still smaller quantity of butyric acid.

The *oxime* of methyl hexyl ketone, $NOH{:}CMe\cdot[CH_2]_5\cdot CH_3$, is an oil, boiling at 213—217° under a pressure of 713 mm. with slight decomposition; when treated in the manner described above, it yields hexylamine, and a very much smaller quantity of methylamine, acetic acid, and a very little heptylic acid; it may, therefrom, be concluded that the principal constituent of this oxime is the stereoisomeride of the configuration $Me\cdot\overset{\|}{C}\cdot C_6H_{13}$ $N\cdot OH$.

The oxime of methyl isopropyl ketone yields propylamine and acetic acid as the principal products, only small quantities of methylamine and isobutyric acid being formed.

It is, of course, at present impossible to say whether the two stereoisomeric forms are actually present in the original oxime, or whether a single modification is partially converted into its stereoisomeride under the conditions employed in these experiments. The results show, however, that the nature of the alcohol radicles has a certain influence on the relative stability of the two theoretically possible configurations, a methyl group having a greater repellent action on the hydroxyl group than the other fatty alcohol radicles; for this reason, in the case of oximes of the general formula

$$NOH{:}CMe\cdot C_nH_{2n+1},$$

the configuration $Me\cdot\overset{\|}{C}\cdot C_nH_{2n+1}$ $N\cdot OH$ is more readily assumed than the configuration $Me\cdot\overset{\|}{C}\cdot C_nH_{2n+1}$ $OH\cdot N$. (See Smith, this vol., p. 487). F. S. K.

α-Bromisovaleric Acid, Pimelic Acid, and Synthesis of Teraconic Acid. By B. Schleicher (*Annalen*, **267**, 114—133).—α-Bromisovaleric acid, prepared by treating isovaleric acid with bromine and amorphous phosphorus, and decomposing the product with boiling water, crystallises from ether and chloroform in lustrous prisms, melts at 44°, and boils at 230° under the ordinary pressure with slight decomposition (at 150° under a pressure of 40 mm. without decomposition). The potassium, ammonium, and sodium salts are readily soluble, do not crystallise, and are unstable in boiling aqueous solution; the barium, strontium, cadmium, and zinc salts are gum-like compounds. The *copper* salt, $(C_5H_8BrO_2)_2Cu$, crystallises in green plates; the *lead* salt, with 1 mol. H_2O, and the *calcium* salt, with 2 mols. H_2O, are crystalline. The *methyl* salt, $C_5H_8BrO_2Me$, prepared by treating the bromide of the acid with methyl alcohol, is a colourless liquid of sp. gr. 1·353 at 13°/13°, boiling at 174°. The ethyl salt boils at 186°, and its sp. gr. is 1·2776 at 12°/12°.

Ethyl α-carboxyethylpimelate, $CHMe_2\cdot CH(COOEt)\cdot CH(COOEt)_2$, prepared as described by Roser (Abstr., 1884, 423), is a heavy oil,

boiling at 276—278)°. α-Carboxypimelic acid, obtained by hydrolysing the ethyl salt with concentrated potash, melts at 160° with evolution of carbonic anhydride, and is readily soluble in water, alcohol, and ether, but more sparingly in chloroform and light petroleum. The *barium* salt, $(C_8H_9O_6)_2Ba_3$, and the *silver* salt, $C_8H_9O_6Ag_3$, are amorphous.

Pimelic acid, prepared by heating the α-carboxy-derivative, melts at 114°; its *strontium* salt, $C_7H_{10}O_4Sr$, is readily soluble in cold, but almost insoluble in boiling water. *Bromopimelic acid* was obtained as a syrup by treating pimelic acid with bromine and amorphous phosphorus; its *ethyl* salt, $C_{11}H_{19}BrO_4$, boils at 248—252° with slight decomposition, but distils unchanged at 165—167° under a pressure of 40 mm.; its *lead* salt, $C_7H_9BrO_4Pb$, and its *calcium* salt, $C_7H_9BrO_4Ca$, are sparingly soluble in water. When ethyl bromopimelate is heated with anhydrous sodium acetate at 180°, and the product hydrolysed with potash, teraconic acid is obtained.

Hydroxypimelic acid (*isopropylmalic acid*),

$$COOH{\cdot}CHPr^{\beta}{\cdot}CH(OH){\cdot}COOH,$$

can be obtained by heating ethyl bromopimelate with potash; it crystallises from ether in lustrous plates melting at 154°. The *calcium* salt, $C_7H_{10}O_5Ca$, is crystalline, but the *lead* salt, $C_7H_{10}O_5Pb$, is amorphous. F. S. K.

The Specific Gravity of Japan Wax. By O. Kleinstück (*Chem. Zeit.*, **14**, 1303—1304).—Determinations of the temperature at which Japan wax, as well as common wax, has the same sp. gr. as water showed that its expansion coefficient was greater than that of water, and that consequently, pieces of the wax sank in water at low temperatures, whilst, at temperatures above a certain point, they floated on the surface. By cutting small blocks of different specimens and allowing the temperature of the water to rise or fall very gradually, in order to give the wax time to assume the temperature of the water, the exact temperature could be determined at which the wax had the same sp. gr. as the water.

The author has also observed that after being recently melted (and after again solidifying), wax has the same density as water at a lower temperature than when some little time has elapsed since being melted. Three specimens were experimented with in 1888. Before being melted, this particular temperature was 17°, 17°, and 18° for the three specimens respectively, whilst, after being melted, the temperature of equal density was 11° for all three specimens.

In 1889, the temperature of equal density for three specimens was, before being melted, 15·9°, 15·3°, and 16·9°, whilst, after melting, the particular temperature was 10·8°, 13·4°, and 14·3° respectively. Determinations were made with three other specimens in 1889—1890. On August 1st, 1889, Specimen 1 had the same density as water at 16·2°; August 2nd, directly after melting and again solidifying, the temperature was 8°; August 17th, 12·3°; September 18th, 14·1°; March 2nd, 1890, 16·0°. The temperature of equal density for Specimen 2 was, for the same dates, 16·2°, 10·5°, 14·3°, 15·5, and

16·0°, whilst the corresponding readings for Specimen 3 were 17·5°, 12·7°, 15·7°, 17·4°, and 17·8°. On March 3rd, 1890, all three specimens were again melted, and after solidifying, the temperatures were 8·4°, 10·3°, and 11·3° for the three specimens respectively, whilst, on July 7th, 1890, the temperatures were 19·0°, 19·3°, and 20·2° respectively. Wax would appear to assume its normal density only very slowly after being melted. J. W. L.

Stereometric Relations of Erucic Acid and Brassidic Acid. By A. Holt (*Ber.*, **24**, 4120—4129).—Erucic acid and brassidic acid are not affected by heating under pressure with sodium amalgam or sodium in alcoholic solution, nor are they changed by heating with alcoholic potash at 150°.

Erucic acid dichloride, $C_{22}H_{42}Cl_2O_2$, is prepared by the action of chlorine on erucic acid, dissolved in chloroform; it crystallises from chloroform in small, lustrous plates melting at 46°. The *methyl salt*, $C_{21}H_{41}Cl_2{\cdot}COOMe$, melts at 30·5°.

Brassidic acid dichloride, $C_{22}H_{42}Cl_2O_2$, resembles the corresponding erucic acid derivative, and melts at 65°. The *methyl salt* melts at 42·5°.

On heating the dichloro-acids with sodium or sodium amalgam in alcoholic solution, the original acids are regenerated, whilst by the action of alcoholic potash in excess for 8—10 hours at 120—130°, monochlorinated substitution products are formed.

Chlorerucic acid, $C_{22}H_{41}ClO_2$, is prepared from brassidic acid dichloride, and melts at 37·5°. *Chlorobrassidic acid*, $C_{22}H_{41}ClO_2$, obtained from erucic acid dichloride, melts at 42°.

Bromerucic acid crystallises in colourless, lustrous needles which melt at 41·5°. The *methyl salt* melts at 18—19°.

Bromobrassidic acid, $C_{22}H_{41}BrO_2$, melts at 34°.

The above mono-haloïd acids are converted into erucic and brassidic acids respectively by the action of sodium in alcoholic solution.

The isomerism of erucic and brassidic acids is thus shown to have been correctly explained by J. Wislicenus; they are represented by the formulæ $\begin{matrix} X{\cdot}C{\cdot}H \\ \| \\ H{\cdot}C{\cdot}COOH \end{matrix}$ and $\begin{matrix} X{\cdot}C{\cdot}H \\ \| \\ COOH{\cdot}C{\cdot}H \end{matrix}$ respectively, since behenolic acid is much more readily formed from the di-haloïd compounds of erucic acid than from those of brassidic acid. J. B. T.

γ-Trichloro-β-Hydroxybutyric Acid. A New Synthesis of Malic Acid. By K. Garzarolli-Thurnlackh (*Monatsh.*, **12**, 556—565).—Chloral and malonic acid in molecular proportion were placed with an excess of acetic acid in a reflux apparatus, and heated in a water-bath for 25—40 hours, until carbonic anhydride was no longer evolved. The product was distilled until the temperature registered 124°, whereby acetic acid and chloral passed over. The residue was dissolved in water, and the yellow solution thus obtained treated with animal charcoal and concentrated until a crystalline mass of the sole product, *γ-trichloro-β-hydroxybutyric acid*, $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, formed. It is readily soluble in hot water and in methyl and ethyl alcohols; dissolves sparingly in chloroform and ether; melts at

118·5°; does not reduce Fehling's solution; is optically active, and may be distilled unchanged in a vacuum. The *calcium salt*, $2(C_4H_4Cl_3O_3)_2Ca + 9H_2O$, is soluble in alcohol, and crystallises from water in slender, white needles; the *silver salt*, $C_4H_4Cl_3O_3Ag$, crystallises from water in long needles, and is decomposed with formation of silver chloride on long-continued boiling of its aqueous solution; the *methyl salt*, $C_4H_4Cl_3O_3Me$, crystallises from methyl alcohol in large, glistening plates, and melts at 61·2—61·6°; and the *acetyl derivative*, $C_4H_4Cl_3O_3Ac$, crystallises from chloroform in small, silky needles, has a characteristic odour, dissolves readily in alcohol and ether, and melts at 86—87°.

When γ-trichloro-β-hydroxybutyric acid is treated with concentrated solutions of potash or baryta, it is converted into malic acid. The calcium salt of the acid thus obtained appears to be identical with that of the malic acid prepared by Loydl (*Annalen*, **192**, 80) from fumaric acid. G. T. M.

Stereoisomeric Dimethyladipic Acids and Dimethylpimelic Acids. By N. Zelinsky (*Ber.*, **24**, 3997—4005).—*Ethyl dimethyldicyanoadipate*, COOEt·CMe(CN)·CH_2·CH_2·CMe(CN)·COOEt, is formed by the action of ethylene bromide on ethyl sodio-α-cyanopropionate; it boils at 300—310° with slight decomposition.

Two isomeric dimethyladipic acids of the constitution

COOH·CHMe·CH_2·CH_2·CHMe·COOH,

are obtained when the preceding compound is boiled with moderately concentrated sulphuric acid until the evolution of carbonic anhydride ceases; the two compounds are separated by fractional crystallisation from water. The more sparingly soluble acid forms monoclinic crystals, melts at 140—141°, and boils at 320—322°, yielding a distillate which has the same melting point as the original acid, but which has an odour of menthol; 100 parts of water at 22° dissolve only 0·5664 gram of the acid, and it is only sparingly soluble in chloroform and ether. The *silver* salt, $C_8H_{12}O_4Ag_2$, is a crystalline, unstable compound.

The more readily soluble dimethyladipic acid forms rhombic crystals, melts at 74—76°, and boils at 320—322°, the distillate having an odour of menthol; it is readily soluble in alcohol, ether, and chloroform, and 100 parts of water at 15° dissolve 6·7 grams of the acid. When heated with hydrochloric acid at 220°, it is converted into the isomeride. The *silver* salt, $C_8H_{12}O_4Ag_2$, is crystalline. Molecular weight determinations in glacial acetic acid solution showed that both acids have the molecular formula $C_8H_{14}O_4$; they have the same electrical conductivity, namely, $k = 0·0042$.

Ethyl dimethyldicyanopimelate, $CH_2[CH_2·CMe(CN)·COOEt]_2$, can be obtained by treating ethyl sodio-α-cyanopropionate with trimethylene bromide; it boils at 220—240° under a pressure of 40—50 mm., and on hydrolysis with concentrated potash it is converted into a liquid acid. When this acid is boiled with concentrated sulphuric acid for some time, it is converted into an oil, from which crystals of dimethylpimelic acid, $C_9H_{16}O_4$, are gradually deposited on

long keeping; after recrystallisation from hot water, this acid melts at 71—73°. The oily mother liquors from the crystalline acid possibly consist of a liquid isomeride. F. S. K.

Note by Abstractor.—The author has evidently overlooked the fact that dimethylpimelic acid has been previously described by Kipping and Mackenzie (Trans., 1891, 569), and also by Perkin and Prentice (*ibid.*, 818).

Condensation of Cyanides with Ethereal Salts. By H. Fleischhauer (*J. pr. Chem.* [2], **44**, 571—572).—*Ethyl cyanopyruvate oxime*, $CN{\cdot}CH_2{\cdot}C(NOH){\cdot}COOEt$, obtained from ethyl oxalate, methyl cyanide, and hydroxylamine, crystallises from hot water in colourless prisms, melts at 104°, and dissolves easily in alcohol and hot water, but not in ether; when heated with strong hydrochloric acid at 125° in a sealed tube, carbonic anhydride and ammonia, but no hydroxylamine, are formed; the *silver* compound was obtained.

The corresponding *hydrazone*, $CN{\cdot}CH_2{\cdot}C(N_2HPh)COOEt$, crystallises from absolute alcohol both in small, white prisms, and in large crystals, and from light petroleum in slender needles; it melts above 100°, and is easily soluble in alcohol and ether, but not in water. A. G. B.

Diiodoacetylenedicarboxylic Acid and Diiodoacrylic Acid. By P. Bruck (*Ber.*, **24**, 4118—4120, and **25**, 503).—Diiodoacetylenedicarboxylic acid, $COOH{\cdot}CI{:}CI{\cdot}COOH$, is prepared by heating acetylenedicarboxylic acid and iodine in molecular proportion with alcohol in a sealed tube for 5—6 hours at 100°, the product is freed from iodine, washed with benzene, and crystallised from a mixture of ether and benzene; it is deposited in small, needle-shaped crystals, melting at 192° with decomposition. The *sodium* and *potassium salts* are hygroscopic; the *silver salt* is amorphous; the *barium salt*, $C_4O_4I_2Ba + 3H_2O$, is crystalline.

Diiodoacrylic acid (propargylic acid diiodide), $CHI{:}CI{\cdot}COOH$, is obtained by heating propargylic acid and iodine in molecular proportion in chloroform solution in a sealed tube for 5—6 hours at 100°; it crystallises from chloroform in colourless prisms, and melts at 104°. The *silver salt* forms small, lustrous plates, and on heating at 100°, yields acetylene iodide. In the later communication (*Ber.*, **25**, 503), the author states that he had overlooked the preparation of this acid by Homolka and Stolz (Abstr., 1885, 1198). J. B. T.

Ethyl Acetonedicarboxylate. By H. v. Pechmann (*Ber.*, **24**, 4095—4104).—The existence of a dipotassium derivative (Abstr., 1890, 673), and the formation of ethyl methylacetonedicarboxylate (*loc. cit.*) from the silver derivative of ethyl acetonedicarboxylate (see below), leads the author to the view that ethyl acetonedicarboxylate has a ketone formula; its behaviour towards acetic chloride is also not in harmony with the alternative hydroxy-formula. Acetic chloride has no action on ethyl acetonedicarboxylate, but the

corresponding acid reacts with 2 mols. of acetic chloride or acetic anhydride, forming a compound which may be regarded as carboxydehydracetic acid; further experiments are, however, in progress on this reaction. The author does not consider that the fact cited by Nef, that ethyl acetoacetate combines with bromine, is a proof that it contains a doubly-linked carbon atom, and he draws attention to Linnemann's observation (*Annalen*, **125**, 307) that acetone forms an additive compound with bromine.

When ethyl potassioacetonedicarboxylate is dissolved in water (15 parts) and a slight excess of silver nitrate dissolved in water (20 parts) added, a crystalline pulp of the *silver derivative* is obtained; after remaining for 20 minutes in the dark, it is collected and washed successively with water, alcohol, and ether; it has the composition $C_9H_{13}AgO_5$, and is very sensitive towards light. When the last-mentioned compound is heated in a reflux apparatus for a quarter of an hour with methyl iodide, ethyl methylacetonedicarboxylate (Abstr., 1890, 673) is obtained, and this condenses with resorcinol in the presence of sulphuric acid with the formation of ethyl *αβ-dimethylumbelliferonecarboxylate*, $COOEt\cdot CH_2\cdot C\leqslant^{C_6H_3(OH)}_{CMe—CO}>O$, which crystallises from dilute alcohol in colourless, lustrous needles, and melts at 140°; it yields the corresponding *carboxylic acid* on boiling with 15 per cent. sodium hydroxide solution; this crystallises from dilute alcohol in colourless, felted needles, melts at 186—188°, and gives *β*-dimethylumbelliferone (Abstr., 1884, 67) when heated in an oil-bath at 200°. A. R. L.

Hydrochelidonic Acid or Acetonediacetic Acid. By J. Volhard (*Annalen*, **267**, 48—106; compare Abstr., 1890, 30).—Further experiments have proved that hydrochelidonic acid (acetonediacetic acid) has the constitution previously assigned to it; the constitution of the dilactone (termed in this paper the ketodilactone), from which the acid was obtained, is, however, still, to a certain extent, doubtful, since it behaves, in almost all respects, like the anhydride of an acid.

The ketodilactone (m. p. 69°, not 75°) dissolves in concentrated hydrobromic acid and in concentrated hydrochloric acid, yielding solutions from which, after a short time, hydrochelidonic acid is deposited in crystals. Lactones, as is well known, are not decomposed by concentrated acids, but anhydrides, such as those of succinic, glutaric, isopropylsuccinic, and phthalic acids, are readily converted into the corresponding acids on treatment with concentrated hydrochloric acid. When the ketodilactone is treated with a concentrated aqueous solution of potassium cyanide, it is quickly converted into the hydrogen potassium salt of hydrochelidonic acid, in which respect also it behaves like an anhydride; under like conditions, the anhydrides of succinic, phthalic, and maleïc acids are converted into the hydrogen potassium salts of the corresponding acids.

Hydrochelidonamic acid, $C_7H_{11}NO_4$, is formed when the ketodilactone is triturated with the theoretical quantity of ammonia, or, better, with well-cooled alcoholic ammonia; in the latter case, the precipi-

tated ammonium salt is washed with chloroform and then decomposed with the theoretical quantity of 50 per cent. acetic acid. It crystallises from alcohol in colourless plates, melts at 127°, and is readily soluble in water and hot alcohol, but only sparingly in acetone, chloroform, and cold alcohol, and almost insoluble in ether, benzene, and light petroleum; it has a strongly acid reaction, decomposes carbonates, and is not decomposed by cold alkalis. The *zinc* salt, $(C_7H_{10}NO_4)_2Zn + 2H_2O$, is crystalline, but most of the other metallic salts could not be obtained in crystals.

Hydrochelidonimide, $C_7H_9NO_3$, is formed when the preceding compound is heated at 145—150° for a long time under the ordinary atmospheric pressure, or, better, for about 30 minutes at 125—130° under reduced pressure (15 mm.). It separates from boiling alcohol in transparent, well-defined, prismatic crystals, melts at 117°, and is readily soluble in chloroform, but only sparingly in ether and benzene, and insoluble in light petroleum and carbon bisulphide; it dissolves freely in water, yielding a strongly acid solution, from which, after warming with zinc carbonate, the zinc salt of hydrochelidonamic acid is obtained on evaporation.

When the dry ammonium salt of hydrochelidonamic acid is gradually heated to about 160°, it is converted into the diimide, $C_7H_{10}N_2O_2$; this substance separates from hot water in colourless, rhombic crystals, $a : b : c = 0{\cdot}8146 : 1 : 0{\cdot}9358$, and is identical with the imidopimelinimide obtained by Marckwald (Abstr., 1888, 677) by the action of alcoholic ammonia on ethyl hydrochelidonate. It is insoluble in benzene, acetone, and light petroleum, and only very sparingly soluble in chloroform, but readily in water, glacial acetic acid, and concentrated hydrochloric acid; when warmed with concentrated potash, it is converted into ammonia and hydrochelidonic acid, but it is not acted on by acid chlorides, acetic anhydride, nitrous acid, hydroxylamine, or reducing agents. The *silver* derivative, $C_7H_8N_2O_2Ag_2$, is a colourless, amorphous substance.

Hydrochelidon-bismethylimide, $C_9H_{14}N_2O_2$, is obtained when the ketodilactone (1 mol.) is treated with an alcoholic solution of methylamine (2 mols.), the solution evaporated over sulphuric acid, and the residue gradually heated to 160°. It crystallises from boiling alcohol in thin, lustrous plates, sinters together at 135°, and melts completely at 140—141°; it is very readily soluble in water, ether, chloroform, and ethyl acetate, and is not decomposed by boiling alkalis, but when fused with potash it yields methylamine.

Hydrochelidonanilic acid, $NHPh{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed, together with the dianilide, when the ketodilactone is heated with aniline at 120—130°; after treating the crystalline product with chloroform to free it from aniline and unchanged ketodilactone, the anilic acid is extracted with cold ammonia and reprecipitated with hydrochloric acid. It crystallises from hot water in transparent, lustrous prisms, melts at 138—139° with decomposition, and dissolves freely in alkalis; the *silver* salt, $C_{13}H_{14}NO_4Ag$, is a colourless, seemingly amorphous compound.

The *dianilide*, $CO(CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, is also produced when methyl hydrochelidonate is boiled with aniline for a long time; it

crystallises from hot alcohol in small needles, melts at 186—187°, and is almost insoluble in cold water.

Lach has shown that when phthalic anhydride is treated with an alcoholic solution of hydroxylamine, it is converted into phthalylhydroxylamine (Abstr., 1883, 1104); benzoic anhydride, under the same conditions, is converted into dibenzhydroxamic acid.

Hydrochelidonic acid dioxime, $C_7H_{10}N_2O_4$, is formed when the ketodilactone is treated with a well-cooled alcoholic solution of hydroxylamine; it crystallises from water in monosymmetric plates, $a : b : c = 1{\cdot}9672 : 1 : 1{\cdot}3614$; $\beta = 88° 52'$, containing 2 mols. H_2O, both of which are expelled at 100°. It crystallises from alcohol in anhydrous needles, which begin to darken at 230° and decompose on further heating, but without melting; it dissolves freely in hot water, soda, and hydrochloric acid, but is only sparingly soluble in warm alcohol, and insoluble in chloroform, acetone, light petroleum, carbon bisulphide, and benzene. Its aqueous solution has a feebly acid reaction, but has no action on carbonates; when the dioxime is boiled with concentrated hydrochloric acid, it is decomposed into hydroxylamine and hydrochelidonic acid. The *diacetyl* derivative, $C_7H_{10}N_2O_5Ac_2$, prepared by warming the dioxime with acetic anhydride, crystallises from hot alcohol in lustrous prisms, melts at 195—196°, and is soluble in acetone, chloroform, glacial acetic acid, and methyl alcohol, but insoluble in ether, benzene, and toluene; it dissolves freely in hot water, but seems at the same time to undergo decomposition, the solution having an acid reaction; its constitution is probably represented by the formula $CO[CH_2{\cdot}CH_2{\cdot}C(OAc){:}NOH]_2$, and that of the dioxime by the formula $\begin{matrix}CH_2-CH_2\\ |\\ C(NOH)\cdot O\end{matrix}>C<\begin{matrix}CH_2-CH_2\\ |\\ O\cdot C(NOH)\end{matrix}>$.

These experiments having left the constitution of the ketodilactone still undecided, the author examined the behaviour of pimelic acid with acetic chloride, acetic anhydride, and phosphorus pentachloride; as, under various conditions, the pimelic acid remained unchanged, and as, moreover, its constitution is very similar to that of hydrochelidonic acid, it follows that the reason why hydrochelidonic acid readily loses the elements of water must be sought for in the presence of the carbonyl group, or, in other words, that the ketodilactone is not an anhydride, but a dilactone of the constitution

$$\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CO-\!-O\end{matrix}>C<\begin{matrix}CH_2{\cdot}CH_2\\ |\\ O-CO\cdot\end{matrix}$$

The true analogues of such a compound would be, not the ordinary dilactones, but the oxetones; it is necessary, therefore, to obtain some evidence that the oxetones have the constitution assigned to them by Fittig (Abstr., 1890, 866) before any conclusions regarding the constitution of the ketodilactone can be drawn from analogy; this evidence is afforded by the synthesis of dimethyloxetone in the following manner:—

Ethyl diallylacetonedicarboxylate, $C_{15}H_{22}O_5$, can be obtained by treating ethyl acetonedicarboxylate with sodium ethoxide and allyl bromide; it boils at 185—186° under a pressure of 10 mm. with slight

decomposition, and on treatment with bromine in carbon bisulphide solution, it yields a brown oil with evolution of hydrogen bromide.

Diallylacetonedicarboxylic acid, prepared by hydrolysing the ethyl salt with alcoholic potash in the cold, crystallises in slender needles melting at 96° with evolution of carbonic anhydride.

Diallylacetone, $C_9H_{14}O$, is obtained when the dicarboxylic acid is heated for some time at 100°, and also when ethyl diallylacetonedicarboxylate is hydrolysed with warm alcoholic potash; it is a colourless oil, boils at 185—186° (at 116° under a pressure of 70 mm.), and combines with hydroxylamine and with phenylhydrazine, yielding oily products. When treated with hydrobromic acid at 0°, it is converted into a dibromide of the composition $C_9H_{16}OBr_2$, identical with the compound obtained by Fittig and Rasch (Abstr., 1890, 867) by the action of hydrobromic acid on dimethyloxetone; this dibromide is decomposed by hot water, yielding Rasch's dimethyloxetone.

The constitution of dimethyloxetone having been determined by the experiments just described, its peculiar behaviour with acids can be easily explained, and is clearly analogous to that of the ketodilactone. The analogy between the two compounds is, however, even more evident when their methods of formation are studied, the reactions by which the oxetone is produced from 2 mols. of valerolactone being quite similar to those by which the ketodilactone is formed from 2 mols. of succinic anhydride.

The compound of the composition $C_{19}H_{20}N_4O_2$, obtained by Bredt (Abstr., 1890, 864) by treating the ketodilactone with phenylhydrazine, has probably the constitution represented by the formula $CO<\begin{matrix}N(NHPh)\\CH_2—CH_2\end{matrix}>C<\begin{matrix}N(NHPh)\\CH_2—CH_2\end{matrix}>CO$, and may therefore be named *dihydrazidopimelic anhydride*; it is readily soluble in boiling glacial acetic acid, but only sparingly in carbon bisulphide, and almost insoluble in ether, benzene, and light petroleum; it is not acted on by alkalis or dilute acids, and it dissolves in concentrated sulphuric acid with a rose-red coloration. The *diacetyl* derivative, $C_{23}H_{24}N_4O_4$, prepared by treating the dihydrazido-compound with acetic chloride at 100°, crystallises from alcohol in lustrous, seemingly quadratic octahedra, and is readily soluble in warm glacial acetic acid and warm chloroform, but only sparingly in most of the other ordinary solvents; it dissolves in concentrated sulphuric acid, yielding a solution which turns red on shaking or on adding a drop of ferric chloride. The *dibenzoyl* derivative, $C_{33}H_{28}N_4O_4$, sinters together at 100°, but without melting completely, and begins to decompose at 110°. A compound of the composition $C_{23}H_{28}N_4O_2$ is formed when the ketodilactone is heated with asymmetrical ethylphenylhydrazine at 100°; it crystallises from hot methyl alcohol in microscopic octahedra, melts at 220—222°, and dissolves freely in chloroform, but is only moderately easily soluble in hot acetone, and insoluble in ether and light petroleum; its behaviour with concentrated sulphuric acid and ferric chloride, and with acids and alkalis, is the same as that of dihydrazidopimelic anhydride.

That hydrochelidonic acid has a symmetrical constitution is rendered highly probable by the above experiments on the constitution of the

ketodilactone; this view is proved to be correct by the synthesis of the acid from acetonedicarboxylic acid in the following manner:—Ethyl acetonedicarboxylate is treated with sodium ethoxide and ethyl chloracetate, and the product boiled with concentrated hydrochloric acid until the evolution of carbonic anhydride ceases; from the solution obtained in this way, hydrochelidonic acid can be easily isolated.

F. S. K.

The Phenylhydrazonehydrazide of Levulinic Acid. By J. Volhard (*Annalen*, **267**, 106—113).—Bredt's assumption that the hydrazine derivatives of hydrochelidonic acid (compare preceding abstract) and levulinic acid resemble one another in constitution and in their manner of formation (Abstr., 1890, 863) is without foundation, and consequently his conclusion that the two acids are analogously constituted is incorrect.

The hydrazone of levulinicphenylhydrazide described by Bredt can be prepared by warming levulinic acid with phenylhydrazine; it is a colourless, microcrystalline powder, melts at 180·5—181·5°, and is readily decomposed by warm, dilute hydrochloric acid; its constitution is most probably expressed by the formula

$$N_2HPh{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}N_2H_2Ph.$$

Levulinicphenylhydrazoneazobenzene, $C_{17}H_{18}N_4O$, is obtained when an alcoholic solution of the hydrazone of levulinicphenylhydrazide is warmed with yellow mercuric oxide; it crystallises in flat, transparent prisms, melts at 142—142·5°, and is readily soluble in benzene, chloroform, and glacial acetic acid, but only sparingly in light petroleum, and insoluble in water, alkalis, and dilute acids. It is not acted on by boiling alkalis, but it is decomposed by warm cencentrated hydrochloric acid with formation of methylindoleacetic acid, benzene, chlorobenzene, ammonia, aniline, and nitrogen; it has in all probability the constitution represented by the formula

$$N_2HPh{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}N_2Ph.$$

F. S. K.

Stereoisomerism of the Dimethyldihydroxyglutaric Acids. By N. Zelinsky (*Ber.*, **24**, 4006—4017).—A *nitrile* of the constitution $CH_2[CMe(CN){\cdot}OH]_2$ is gradually deposited when hydrochloric acid of sp. gr. 1·19 is added drop by drop to a well-cooled mixture of acetylacetone, potassium cyanide, and water; it separates from hot alcohol and benzene in crystals, melts at 134—136° with decomposition, and is only sparingly soluble in ether.

A *lactone* of *dimethyldihydroxyglutaric acid* (*dimethylhydroxybutyrolactonecarboxylic acid*, $COOH{\cdot}CMe<^{O{\cdot}CO}_{CH_2-}>CMe{\cdot}OH$, is obtained when the preceding compound is treated with hydrochloric acid of sp. gr. 1·19, first at the ordinary temperature and then at 100°, the solution evaporated to dryness, and the residue extracted with ether; it crystallises from water in large, rhombic plates, melts at 189—190°, is optically inactive, and is only sparingly soluble in water and alcohol, but readily in ether. The *barium* salt, $(C_7H_9O_5)_2Ba + 2H_2O$, prepared by treating the lactonic acid with barium carbonate, crystal-

lises in silky needles. When the lactonic acid is boiled with barium hydroxide, the *barium* salt of dimethyldihydroxyglutaric acid, $C_7H_{10}O_6Ba + 2\frac{1}{2}H_2O$, is obtained; this compound is decomposed by acids, the lactonic acid being regenerated; the potassium salt shows a like behaviour.

The *dilactone*, $CMe\begin{<}\begin{matrix}CO\cdot O\\ CH_2\\ O\cdot CO\end{matrix}\end{>}CMe$, is produced when the lactonic acid is distilled; it forms small, colourless crystals, melts at 104—105°, and is readily soluble in ether, alcohol, and benzene, but only moderately easily in hot, and almost insoluble in cold, water. It is not acted on by boiling water, and it dissolves unchanged in concentrated sulphuric acid.

Dimethyldihydroxyglutaric acid, $C_7H_{12}O_6$, can be obtained by boiling the dilactone for a short time with excess of dilute potash, and then acidifying with sulphuric acid; it separates from ether and water in colourless crystals, melts at 103—104°, and is readily soluble in alcohol and hot water, but only moderately easily in ether and cold water. It is probably identical with the acid (m. p. 95—96°) obtained by Auwers and Jackson (Abstr., 1890, 1098) from dibromodimethylglutaric acid. When titrated with very dilute barium hydroxide or potash in the cold, it behaves like a monocarboxylic acid, but at higher temperatures it shows the behaviour of a dicarboxylic acid. The fact that this acid is stable, whilst the dicarboxylic acid which is formed on treating the lactonic acid with alkalis is unstable, leads to the conclusion that dimethyldihydroxyglutaric acid exists in two structurally identical modifications, the configurations of which may be represented by the formulæ

$\begin{matrix}CH_3\\ OH\cdot C\cdot COOH\\ CH_2\\ OH\cdot C\cdot COOH\\ CH_3\end{matrix}$	and	$\begin{matrix}COOH\\ CH_3\cdot C\cdot OH\\ CH_2\\ OH\cdot C\cdot COOH\\ CH_3\end{matrix}$
Unstable acid.		Stable acid.

The stable acid (m. p. 103—104°) is optically inactive, but seems to consist of two optically active modifications; it separates from ether in well-defined crystals, some of which were found to be enantiomorphous. F. S. K.

A New Pentonic Acid and the Second Inactive Trihydroxyglutaric Acid. By E. Fischer and O. Piloty (*Ber.*, **24**, 4214—4225). —It has been shown that when certain monocarboxylic acids of the sugar group are heated with quinoline or pyridine, they are converted into stereoisomeric acids, differing only from the original compounds in the relative position of the carboxyl to the adjacent carbon atom. When arabonic acid, $OH\cdot CH_2\cdot\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot COOH$, is treated by this method, in the manner to be described, it yields a new acid,

$OH\cdot CH_2\cdot\overset{OH}{\overset{|}{C}}H—\overset{OH}{\overset{|}{C}}H—\overset{OH}{\overset{|}{C}}H\cdot COOH$, which the authors name *ribonic acid.*

For this purpose, a 10 per cent. aqueous solution of arabonic acid (600 grams) is heated with pyridine at a maximum temperature of 130°, in a copper autoclave, for three hours, a concentrated solution of barium hydroxide (650 grams) added, and after boiling off the pyridine, and precipitating the barium with a small excess of sulphuric acid, it is treated with lead carbonate (60 grams) mixed with water to a paste, in order to precipitate the excess of sulphuric acid. The solution is then filtered while hot, the filtrate treated with hydrogen sulphide, and the lead sulphide removed by filtration. It is then boiled with an excess of calcium carbonate for half an hour, treated with animal charcoal, and the filtrate evaporated to a thin syrup. This is allowed to remain for 12 hours, when calcium arabonate (400 grams) separates and is removed, whilst the mother liquor is exactly precipitated with oxalic acid, and the filtrate boiled with an excess of cadmium hydroxide for half an hour, treated with animal charcoal, filtered hot, and evaporated to a syrup, from which crude cadmium ribonate (115 grams) separates after a time in cauliflower-like masses, and is crystallised from a small quantity of hot water. When an aqueous solution of the pure salt is treated with hydrogen sulphide, and the filtrate evaporated to a syrup, a crystalline cake of the *lactone*, $C_5H_8O_5$, is obtained; this is dissolved in ethyl acetate (30 parts) by boiling, and the filtrate evaporated to one-third, whereby the lactone separates in long, colourless prisms; it melts at 72—76°, has a neutral reaction, does not reduce Fehling's solution, and is very easily soluble in water, alcohol, and acetone, somewhat sparingly in ethyl acetate, and very sparingly in ether. It has a specific rotatory power $[\alpha]_{D20} = -18$, which remains the same if the solution is examined 12 hours after preparation. The *calcium*, *barium*, and *lead* salts are very readily soluble in water, and leave gummy residues when their solutions are evaporated; the *mercury* salt, obtained by boiling the lactone with water and mercuric oxide, separates from its solution as a jelly, which changes after a time into delicate needles; when basic lead acetate is added to an aqueous solution, the ribonic acid is precipitated. The above-mentioned *cadmium* salt dissolves readily in hot water, and separates quickly on cooling in mammelated groups of delicate needles; its aqueous solutions have a specific rotation $[\alpha]_{D20^\circ} = 0{\cdot}6$. The *phenylhydrazide*, $C_5H_9O_5\cdot N_2H_2Ph$, obtained by heating the lactone, phenylhydrazine, and water (1 gram of each) for an hour on the water-bath, treating the crystalline product with alcohol, and crystallising it from boiling absolute alcohol, forms colourless needles, melts at 162—164°, and decomposes at 180°.

Ribonic acid is distinguished from arabonic acid by the fact that the calcium salt of the latter crystallises well, as also by the difference in the melting points and solubilities of their respective phenylhydrazides (see Abstr., 1890, 1398). Furthermore, the lactone of arabonic acid melts at 98°, and has a specific rotation $[\alpha]_{D20} = -73{\cdot}9$, remaining unaltered after 14 hours; the values given by Bauer

(Abstr., 1886, 869) are too low, as is also the determination of the rotatory power by Allen and Tollens (Abstr., 1891, 669), the latter chemists having evidently dealt with a mixture of the acid and the lactone.

Ribonic acid is converted into arabonic acid when the lactone of the former (2 grams) is heated with water (10 grams) and pyridine (1·5 grams) in a sealed tube at 130—135° for three hours; it is then converted first into the barium and subsequently into the calcium salt, the yield being 1 gram of the salt.

Ribose.—When to a 10 per cent. aqueous solution of ribonic lactone, cooled to its freezing point, $2\frac{1}{2}$ per cent. sodium amalgam is added by degrees with vigorous shaking, the solution being kept acid by the addition of dilute sulphuric acid, the reduction proceeds quickly, and after adding a quantity of the amalgam corresponding with 10 times the weight of the lactone, the operation is stopped, and the solution decanted from the mercury. It is then made alkaline, the filtrate exactly neutralised with sulphuric acid in the cold, and absolute alcohol (6 parts) added, whereby the whole of the sodium sulphate and a portion of the unattacked sodium arabonate are precipitated. To the filtrate, 20 per cent. basic lead acetate solution is added as long as a precipitate is formed, and an excess of basic lead acetate to this filtrate, and then concentrated baryta solution until precipitation is complete. The precipitate, which contains the chief portion of the ribose, is carefully washed with water, and decomposed with very dilute sulphuric acid, filtered, and exactly precipitated with baryta; the filtrate from this, on evaporation, yields the sugar as a colourless syrup, containing only a small quantity of inorganic matter; a considerable quantity of furfuraldehyde is also formed.

When equal quantities of the last-mentioned syrup and phenylhydrazine are mixed with a very small quantity of absolute alcohol and allowed to remain for 12 hours, the *phenylhydrazide* separates on adding ether as a brownish syrup which solidifies after a time, and crystallises from alcohol in colourless crystals, sinters at 150°, melts at 154—155°, with gradual decomposition, and is very readily soluble in water. The *parabromophenylhydrazide*, $C_{11}H_{15}O_4BrN_2$, separates when the sugar is boiled with absolute alcohol and parabromophenylhydrazine for 12 hours. The product, after washing with ether, crystallises from alcohol as a colourless crystalline powder, melts at 164—165° with gradual decomposition, and is readily soluble in water. The *osazone* was also prepared, and appears to be identical with that obtained from arabinose, a result which was to be anticipated.

Ribonic acid is converted into trihydroxyglutaric acid as follows:—The lactone (10 grams) is heated in a platinum dish with nitric acid, sp. gr. 1·2 (25 c.c.), for 20—25 minutes on the water-bath with constant stirring; the product is added to water (160 c.c.), neutralised with calcium carbonate, treated with animal charcoal, and filtered while hot, whereby a portion of the calcium trihydroxyglutarate separates on cooling as a yellow, crystalline powder, and a further yield is obtained on evaporating the filtrate to one-third in a partial vacuum; whilst another portion separates on allowing the mother liquor to remain in the cold for several days, the entire yield

being 4·5 grams. When the calcium salt is digested with a hot solution containing the calculated quantity of oxalic acid, and the filtrate evaporated under diminished pressure at 60°, the *lactone*, $C_5H_6O_6$, is obtained; it separates from a concentrated solution in ethyl acetate in nodules consisting of aggregates of small needles, melts when quickly heated at 170—171°; it is very readily soluble in water and alcohol, fairly in acetone, somewhat sparingly in ethyl acetate, but almost insoluble in ether; it is optically inactive. When boiled with hydriodic acid and amorphous phosphorus for four hours, it is converted into glutaric acid. The acid corresponding with the last-described lactone may be represented by the configuration

$$\begin{array}{c} \dot{O}H\ \dot{O}H\ OH \\ COOH\cdot\dot{C}-\dot{C}-\dot{C}\cdot COOH. \\ \dot{H}\ \ \dot{H}\ \ \dot{H} \end{array}$$

The isomeric trihydroxyglutaric acid, $\begin{array}{c} \dot{O}H\ \dot{H}\ \ OH \\ COOH\cdot\dot{C}-\dot{C}-\dot{C}\cdot COOH \\ \dot{H}\ \ \dot{O}H\ \dot{H} \end{array}$, from xylose exhibits no tendency to form a lactone, even when its aqueous solution is evaporated under diminished pressure or at the ordinary pressure; when crystallised from ethyl acetate, it melts at 152°, instead of 145·5° as previously stated (Abstr., 1891, 1177), and yields a potassium salt, $C_5H_6O_7K_2 + 2H_2O$, which crystallises well; whereas a crystalline potassium salt could only be obtained from the isomeric acid from ribose with difficulty. The difference of the two trihydroxyglutaric acids appears therefore to be beyond doubt.

A. R. L.

Action of β-Iodopropionic Acid on Ethyl Thiocarbamate. By N. A. Langlet (*Ber.*, **24**, 3848—3853).—*Carbamine-β-thiolactic acid*, $NH_2\cdot CO\cdot S\cdot CH_2\cdot CH_2\cdot COOH$, is obtained by heating ethyl thiocarbamate (10·5 grams) with β-iodopropionic acid (20 grams) until gas begins to be evolved; the reaction then takes place without further heating, and ethyl iodide distils over. The product is poured into a dish and allowed to cool, and the solid compound thus obtained crystallised from hot water and washed with ether. It crystallises from water in white, lustrous leaflets, melts at 147·5°, and tastes and reacts acid. When oxidised in hydrochloric acid solution with potassium chlorate, it yields β-sulphonepropionic acid. The *alkali* salts are very hygroscopic, and were not obtained pure; by excess of alkali, it is very easily decomposed into thiolactic acid, carbonic acid, and ammonia. The *calcium* salt, $(NH_2\cdot CO\cdot S\cdot C_2H_4\cdot COO)_2Ca,3H_2O$, is obtained by neutralising a solution of the acid with calcium carbonate; it crystallises in pure white needles, is very soluble in water, insoluble in alcohol, loses its water of crystallisation at 100°, and easily decomposes above that temperature. The *barium* salt crystallises with 2 mols. of water, has similar properties to the calcium salt, but is not stable in solution. The *silver* salt,

$$NHAg\cdot CO\cdot S\cdot C_2H_4\cdot COOAg,$$

is obtained as a yellowish-white precipitate on adding silver nitrate to a solution of the acid.

Sinapanpropionic acid, $NH<^{CO\,—\,S}_{CO\cdot CH_2}>CH_2$, is obtained by heating ethyl thiocarbamate (10·5 grams), β-iodopropionic acid (20 grams), and acetic anhydride (10 grams) until reaction sets in. The acetic acid is evaporated off on the water-bath; the mixture allowed to cool, the semi-solid mass mixed with ether, and the crystals separated and crystallised from hot water. It forms short, colourless needles or rhombic plates, melts at 159°, sublimes unchanged, and is easily soluble in hot water, but only sparingly so in cold. The solution has a neutral reaction; the acid properties of the compound are shown by the ease with which it dissolves in cold potash. When heated with excess of potassium hydroxide, it does not yield thiolactic acid. When boiled with mercuric oxide, the sulphur is not eliminated, but the chain is broken with formation of the mercaptide of β-thiolactic acid.

Carbaminethiolactic acid is also obtained in small quantity on boiling an alcoholic solution of β-iodopropionic acid with potassium thiocyanate, and hydrolysing the product by boiling with hydrochloric acid. In an experiment in which the boiling with hydrochloric acid was continued for some time, a small quantity of sinapanpropionic acid was also formed.

Although it is not possible to obtain a closed-chain compound from carbamide and β-iodopropionic acid, the author has obtained a compound which he believes to have the formula $CH_2<^{S\cdot C(NH_2)}_{CH=CH}>N$ or $CH_2<^{S\cdot C(NH)}_{CH=CH}>NH$, by employing the aldehyde in place of the acid. The substance, which is difficult to purify, is sparingly soluble in water, easily so in acids, and gives insoluble precipitates with platinic and mercuric chlorides. The further description of this compound is reserved for a later date. E. C. R.

Silver Compound of Thiocarbamide. By N. Kurnakow (*Ber.*, **24**, 3956—3962; compare Reynolds, Trans., 1892, 249).—The author finds that the compound described by Reynolds (*Annalen*, **150**, 235) as the silver compound of thiocarbamide, $Ag_2O,2CSN_2H_4 + 4H_2O$, consists of a mixture of double compounds of the general formula $AgNO_3,nCSN_2H_4$, n being 1, 2, or 3. The compound $AgNO_3,CSN_2H_4$ may be obtained pure by pouring a solution of thiocarbamide into one containing an excess of silver nitrate, and recrystallising the precipitate from water containing silver nitrate and nitric acid. It dissolves readily in a solution of thiocarbamide on warming, and on slow cooling the compound $AgNO_3,3CSN_2H_4$ separates out in white crystals. On adding an excess of hydrochloric acid to the solution of the last compound, a white, crystalline precipitate is formed, which separates from aqueous thiocarbamide in prismatic crystals, and is identical with the double compound of silver chloride and thiocarbamide, $AgCl,2CSN_2H_4$, described by Volhard (this Journ., 1874, 574) and Baumann (this Journ., 1875, 632).

The author has found that the supposed compounds of thiocarbamides with mercuric oxide likewise contain nitric acid, and believes

that these have a constitution similar to the silver compounds. He regards the existence of any compounds of thiocarbamides with oxides as extremely doubtful. H. G. C.

Alloxanhydrazone. By O. Kühling (*Ber.*, **24**, 4140—4145).—*Alloxanhydrazone*, $CO<^{NH\cdot CO}_{NH\cdot CO}>C{:}N\cdot NHPh$, is prepared by the addition of phenylhydrazine hydrochloride to alloxan or alloxantin in hot aqueous solution; a considerable evolution of nitrogen occurs, and the hydrazone separates in the form of a voluminous, yellow precipitate; the purification of the compound is a matter of some difficulty, and is best accomplished by repeatedly boiling with water, dissolving the residue in glacial acetic acid, adding hydrochloric acid, and heating the solution for several hours in a reflux apparatus; the crystals which separate on cooling this solution are then extracted several times with boiling water. The compound melts at 298—300°, and readily dissolves in alkalis and alkali carbonate solutions; it is not hydrolysed by heating with acids.

Dimethylalloxanhydrazone, $CO<^{NMe\cdot CO}_{NMe\cdot CO}>C{:}N\cdot NHPh$, is obtained in a similar manner to the preceding compound, by the action of phenylhydrazine hydrochloride on tetramethylalloxantin; it is deposited from glacial acetic acid in slender, yellow crystals melting at 261°, and is insoluble in alkalis.

On heating alloxanphenylhydrazone with sodium carbonate solution until the red colour disappears and then acidifying with hydrochloric acid, *glyoxalylamidoformic acid phenylhydrazone*,

$$NHPh\cdot N{:}CH\cdot CO\cdot NH\cdot COOH,$$

is obtained; it crystallises from dilute alcohol, is soluble in alkalis, melts at 169°, and rapidly oxidises on exposure to air.

Dimethylalloxanphenylhydrazone yields a compound of the formula $NHPh\cdot N{:}CH\cdot CO\cdot NMe\cdot CO\cdot NHMe$ by the action of sodium carbonate; it crystallises from dilute alcohol containing a little hydrochloric acid in pale-yellow needles, melts at 123—124°, and is insoluble in alkalis. J. B. T.

Condensation of Levulinic Acid with Furfuraldehyde. By E. A. Kehrer (*Ber.*, **24**, 4104—4105).—The statement recently put forward by Erdmann that the author and Ludwig do not wish to reserve this subject for themselves is incorrect. A. R. L.

β-Isopropylthiophen. By A. Thiele (*Annalen*, **267**, 133—138).—*β-Isopropylthiophen*, $C_7H_{10}S$, prepared from sodium isopropylsuccinate by Volhard and Erdmann's method, is a colourless, mobile, highly refractive liquid, having an odour like that of benzene. It boils at 157—158° under a pressure of 754 mm., and is insoluble in water, but miscible with the ordinary organic solvents; it gives the indophenine reaction.

β-Isopropylacetothienone, C_7H_9AcS, is obtained when aluminium chloride is added in small portions at a time to a solution of isopro-

pylthiophene and acetic chloride in light petroleum, and the mixture warmed on the water-bath until the evolution of hydrogen chloride ceases; it is a yellow oil, boils at 237°, and is readily volatile with steam. The *oxime* crystallises in slender needles. The *hydrazone* crystallises from ether in yellow plates, and darkens on exposure to the air.

β-Isopropylpropiothienone, $C_{10}H_{14}OS$, prepared in like manner, is a yellow oil, boils at 251°, and is readily volatile with steam; on oxidation with potassium permanganate in dilute alkaline solution, it yields a yellow, oily acid, which, from analyses of its salts, is probably β-propylthienylglyoxylic acid, $CS_4H_2Pr{\cdot}CO{\cdot}COOH$. F. S. K.

Action of Dilute Nitric Acid on Nononaphthene. By Konovaloff (*Compt. rend.*, **113**, 1052—1053).—The nononaphthene, C_9H_{18}, which the author found some years ago to be identical with hexahydropseudocumene, is easily nitrated by heating with dilute nitric acid (sp. gr. 1·16 to 1·03) in sealed tubes, at temperatures varying from 110° to 150°, according to the strength of the acid. The chief product is *nitronononaphthene*, $C_9H_{17}{\cdot}NO_2$, which boils at 131—133° under a pressure of 40 mm., and at 224—227° with partial decomposition under atmospheric pressure. Its specific gravity is 1·0062 at 0°/0° and 0·9908 at 20°/0°. It dissolves very sparingly in concentrated potash, and is reprecipitated from this solution by water. It gives a pale-green colour with nitrous acid, owing, perhaps, to the formation of the pseudonitrole. When heated with a mixture of nitric and sulphuric acids, it is decomposed with the formation of a base. A base is also formed when it is distilled at atmospheric pressure. It is reduced by zinc and acetic acid to the amidonaphthene and a compound, $C_8H_{16}CO$, which is stated to be a ketone.

Amidonononaphthene, $C_9H_{17}{\cdot}NH_2$, boils at 173—175°. It is a powerful base, as it forms a salt with carbonic anhydride. The *hydrochloride*, $C_9H_{17}{\cdot}NH_2{,}HCl$, crystallises from light petroleum, in which it is sparingly soluble, in cubes, but these, when exposed to the air, are transformed into crystals which act on polarised light and belong to another system. It is soluble also in water, alcohol, ether, and benzene. The *platinochloride*, $(C_9H_{17}{\cdot}NH_2)_2{,}H_2PtCl_6$, is easily soluble in alcohol and warm water, and crystallises from the latter in brilliant, yellow scales. Amidonononaphthene forms a compound with nitrous anhydride which may be converted into an alcohol.

The *ketonic compound*, $C_8H_{16}CO$, which is, perhaps, a homologue of menthone, $C_{10}H_{18}O$ boils at 180—182°, and has a specific gravity of 0·8903 at 0°/0° and 0·8747 at 20°/0°. It is insoluble in water, and has a faint odour, which resembles those of menthol and suberone. It can be reduced to an alcohol, and forms a compound with hydroxylamine, but it does not combine with sodium hydrogen sulphite or phenylhydrazine, or reduce Fehling's or ammoniacal silver solution. The *oxime*, $C_9H_{16}{\cdot}NOH$, is a liquid which boils with partial decomposition at 220—225°; it is soluble in alcohol and acids, and is reconverted into the amine by reduction with sodium in alcoholic solution, and into the ketonic substance by boiling with acids. Jn. W.

Derivatives of Paranitrorthochlorobenzyl Bromide. By O. Witt (*Ber.*, **25**, 77—89).—*Paradinitrorthodichlorostilbene*, $C_2H_2(C_6H_3Cl\cdot NO_2)_2$, is obtained as a yellow, flocculent precipitate by heating a mixture of paranitrorthochlorobenzyl bromide and potassium or sodium hydroxide in molecular proportion, dissolved in alcohol. Parahydrazorthodichlorodibenzyl alcohol is formed at the same time, and remains in solution. It is also obtained by gradually adding alcoholic potash to an alcoholic solution of the bromide until the yellow precipitate begins to turn red; the yield is not so good as that obtained by the first method; and, if the alkali be added too rapidly, parazoxyorthodichlorostilbene is also formed. The yellow precipitate is insoluble in ether, alcohol, light petroleum, benzene, chloroform, carbon bisulphide, and acetone, somewhat soluble in acetic acid, and very easily soluble in hot nitrobenzene. It crystallises in small, yellow needles, and melts at 294°. It does not yield nitroamidodichlorostilbene when treated with tin and hydrochloric acid, or with zinc-dust and acetic acid, and gives resinous products when treated with alcoholic ammonium sulphide. Dinitrodichlorostilbene can also be obtained from paranitrorthochlorotoluene.

Parazoxyorthodichlorostilbene, $O<\begin{matrix}N\cdot C_6H_3Cl\cdot CH\\ \|\\ N\cdot C_6H_3Cl\cdot CH\end{matrix}>$, is prepared by the following methods:—(1) By gradually adding excess of alkali or sodium ethoxide to an alcoholic solution of paranitrorthochlorobenzyl bromide or paranitrorthochlorotoluene and heating the mixture for 8—10 hours in a reflux apparatus; (2) by heating paranitrorthochlorobenzyl ethyl ether or methyl ether with alkali for some time in alcoholic solution; (3) by heating paradinitrorthodichlorostilbene, suspended in alcohol, with excess of alkali, for 8—10 hours in a reflux apparatus. The last two methods give theoretical yields. It is a reddish-brown compound, is only sparingly soluble in alkaline alcohol, insoluble in all other solvents, decomposes above 300°, and partially sublimes. It is purified by extraction with hydrochloric acid, water, nitrobenzene, alcohol, and ether.

Parahydrazorthodichlorodibenzyl alcohol, $N_2H_2(C_6H_3Cl\cdot CH_2\cdot OH)_2$, is contained, as mentioned above, in the mother liquors from the preparation of paradinitrorthodichlorostilbene, and is obtained from them, by steam distillation, as an oil which soon solidifies. It crystallises from alcohol and ether, melts at 35°, is soluble in acetic acid and chloroform, and turns green on exposure to light. It does not show basic properties, does not yield alcohol when treated with concentrated hydrochloric acid, and when heated in a sealed tube with concentrated hydrochloric acid it does not yield a benzidine; neither does it yield a hydrazoïn with benzaldehyde. On reduction, it yields paramidorthochlorobenzyl alcohol.

Paranitrorthochlorobenzyl methyl ether, $NO_2\cdot C_6H_3Cl\cdot CH_2\cdot OMe$, is obtained by dissolving paranitrorthochlorobenzyl bromide and alkali hydroxide or sodium in methyl alcohol in molecular proportion, heating the mixture in a reflux apparatus for one hour, and then distilling the ether with steam. It crystallises in white plates, melts at 54°, is soluble in alcohol, ether, and acetic acid, insoluble in water, and turns pale green on exposure to light.

Paranitrorthochlorobenzyl ethyl ether, $NO_2 \cdot C_6H_3Cl \cdot CH_2 \cdot OEt$, is obtained by heating paranitrorthochlorobenzyl bromide and potassium cyanide, in molecular proportion, with ethyl alcohol, in a sealed tube, for four hours at 100°, and distilling the ether with steam. It crystallises in well-formed needles, melts at 33°, and is soluble in alcohol, ether, chloroform, and acetic acid, insoluble in water. When heated in a sealed tube with concentrated hydrochloric acid, it yields alcohol and paranitrorthochlorobenzyl alcohol.

Paramidorthochlorobenzyl ethyl ether, $NH_2 \cdot C_6H_3Cl \cdot CH_2 \cdot OEt$, is obtained by reducing the preceding compound with tin and hydrochloric acid. It is an oil which does not solidify in a freezing mixture. The *hydrochloride* forms long, white needles, and sublimes at 240° with partial decomposition.

Paranitrorthochlorobenzyl alcohol, $NO_2 \cdot C_6H_3Cl \cdot CH_2 \cdot OH$, is obtained by heating its ethyl ether in a sealed tube with fuming hydrochloric acid for some time at 100°, and is an oil which could not be obtained crystalline.

Paramidorthochlorobenzyl alcohol is obtained by reducing the preceding compound with tin and hydrochloric acid, and is also an oil, but yields crystalline salts. It is also obtained by reducing parahydrazorthodichlorodibenzyl alcohol with tin and hydrochloric acid. The *hydrochloride* crystallises in broad, white needles, turns green on exposure to air, decomposes at 254°, and partially sublimes, and is soluble in water, hydrochloric acid, and alcohol, insoluble in ether.

Paramidorthochlorotoluene, $C_6H_3MeCl \cdot NH_2$, is obtained by reducing paranitrorthochlorobenzyl bromide with tin and hydrochloric acid. It is an oil at ordinary temperatures, crystallises when cooled, and then melts at 26°. The hydrochloride crystallises in white needles, and is soluble in water and alcohol, insoluble in ether.

Paranitrorthochlorobenzylaniline, $NHPh \cdot CH_2 \cdot C_6H_3Cl \cdot NO_2$, is obtained, together with dinitrodichlorodibenzylaniline, by heating paranitrorthochlorobenzyl bromide (1 mol.) with aniline (2 mols.) in alcoholic solution for four hours in a reflux apparatus. On adding water to the mixture, a yellow powder is obtained, from which the nitrochlorobenzylaniline is extracted with hot hydrochloric acid, and, on cooling, the *hydrochloride* crystallises in transparent, white plates, which soon turn red. The free base which may be obtained by treating the hydrochloride with water, crystallises from alcohol in yellow plates, melts at 73°, and is soluble in ether and acetic acid.

Paradinitrorthodichlorodibenzylaniline, $NPh(CH_2 \cdot C_6H_3Cl \cdot NO_2)_2$, is obtained by heating nitrochlorobenzyl bromide and aniline in molecular proportion, dissolved in alcohol, for eight hours in a reflux apparatus. It is purified by extraction with hot hydrochloric acid and crystallisation from acetic acid, forms small, yellow crystals, melts at 172°, and is somewhat soluble in alcohol, ether, and chloroform. It does not give salts with acids.

Paradinitrorthodichlorodibenzylamine, $NH(CH_2 \cdot C_6H_3Cl \cdot NO_2)_2$, is obtained as a white precipitate, together with trinitrotrichlorotribenzylamine by passing ammonia into a boiling alcoholic solution of nitrochlorobenzyl bromide. The precipitate is dissolved in hydrochloric acid, reprecipitated with dilute alkali, and then fractionally

crystallised from alcohol, in which the dibenzylamine is less soluble. It crystallises in white, microscopic needles, melts at 120°, is soluble in alcohol, chloroform, and concentrated acids, with which it forms easily decomposable salts, is sparingly soluble in ether, and insoluble in water. The tribenzylamine was not obtained in a pure condition.

E. C. R.

Condensation of Isoamylene and Cinnamene with Phenols. By W. Koenigs and R. W. Carl (*Ber.*, **24**, 3889—3900).—The condensation was effected by allowing the hydrocarbon and the phenol to remain for four days with a mixture of 1 part of concentrated sulphuric acid with 9 of glacial acetic acid, diluting with water, neutralising with ammonia and ammonium carbonate, decomposing the acetyl compound formed by boiling with aqueous soda, filtering the alkaline solution, acidifying it, distilling over, first, unacted-on phenol with steam at 100°, and, finally, the condensation product with superheated steam at 160—170°. The hydrocarbon adds itself on, if possible, in the para-position to the hydroxyl; probably, also, to some extent in the ortho-position, as paracresol also yields a condensation product.

Isoamylthymol, $OH\cdot C_6H_2MePr^{\beta}\cdot CMe_2Et$ [Me : OH : Pr^{β} : C_5H_{11} = 1 : 3 : 4 : (?)6], obtained by the addition of isoamylene to thymol, melts at 76·5°, and boils at 275° (uncorr.) under 716 mm. pressure. When boiled with water, it has a musk-like odour; it dissolves in dilute alkalis and in the usual organic solvents, and crystallises from light petroleum in magnificent, colourless, transparent, monoclinic prisms ($a : b : c$ = 2·5136 : 1 : 2·4997 ; β = 68° 16′).

The phenylhydroxyphenylethane, $OH\cdot C_6H_4\cdot CHMePh$, obtained by the addition of cinnamene to phenol (Koenigs, Abstr., 1891, 208), was shown to be a para-compound, because its methyl derivative, obtained by boiling the phenol with potash and methyl iodide in methyl alcohol, yields paramethoxybenzophenone when oxidised with potassium dichromate and sulphuric acid.

Phenylorthohydroxytolylethane, $OH\cdot C_6H_3Me\cdot CHMePh$ [Me : OH = 1 : 2], obtained by the addition of cinnamene to orthocresol, forms a yellowish syrup, which decomposes partially when distilled, and dissolves in most solvents, water excepted. The *methyl derivative* forms a yellow oil boiling at 300—310°, dissolves readily in acetone, ether, light petroleum, and chloroform, sparingly in methyl alcohol, very sparingly in water. When oxidised with dilute sulphuric acid and manganese dioxide, it yields *phenyl orthomethoxytolyl ketone*. $OMe\cdot C_6H_3Me\cdot COPh$, identical with the substance obtained by treating the *methyl derivative of orthocresol* (a colourless oil boiling at 165°, uncorr., and smelling like aniseed) with benzoic chloride in the presence of aluminium chloride. It melts at 80°, and crystallises from ether in rhombs or in fine twins, resembling those of staurolite.

Phenylmetahydroxytolylethane, $OH\cdot C_6H_3Me\cdot CHMePh$ [Me : OH = 1 : 3], obtained by the addition of cinnamene to metacresol, crystallises with difficulty; it melts at 124°, decomposes partially when distilled, dissolves readily in most solvents, water excepted, and sparingly in light petroleum. Its *methyl derivative* melts at 63°.

Paracresol and α-naphthol unite with cinnamene, but no crystalline

products could be obtained. β-Naphthol forms a compound with phenylethylene which does not crystallise, but its *benzyl derivative*, $OBz{\cdot}C_{10}H_6{\cdot}CHMePh$, crystallises from dilute alcohol in plates with a pearly lustre, and melts at 138°.

The *benzoyl derivative of β-naphthol* crystallises from hot alcohol in colourless prisms with a silky lustre, from hot light petroleum in spherical aggregates; it melts at 106°. C. F. B.

Synthesis of the Sixth Dihydroxytoluene. By L. Limpach (*Ber.*, **24**, 4136—4140).—*Methoxycresol* [Me : OH : OMe = 1 : 2 : 3] is prepared from the corresponding amidomethoxycresol by means of the diazo-reaction as a viscid liquid which solidifies in a freezing mixture, melts at 39°, and boils at 209° (uncorr.); it is almost insoluble in water, but readily dissolves in alcohol, benzene, ether, and chloroform. The corresponding *ethoxycresol* is obtained in a similar manner to the methoxy-derivative, which it closely resembles, and is an oily liquid boiling at 214° (uncorr.).

Dihydroxytoluene, $C_6H_3Me(OH)_2$ [Me : OH : OH = 1 : 2 : 3], is formed by heating either of the preceding compounds with six parts of fuming hydrochloric acid in a sealed tube for eight hours at 160°; it solidifies at low temperatures, melts at 47°, and boils at 238—240° (uncorr.), undergoing slight decomposition; it is somewhat sparingly soluble in ether, but readily dissolves in water, alcohol, benzene, or chloroform. With ferric chloride, a green coloration is produced which soon disappears; the addition of ammonia changes the green colour to violet. The constitution of the compound is proved by the method of its formation; it differs, however, in properties from isorcinol, but as the latter compound is prepared by the fusion of toluenedisulphonic acid with potassium hydroxide, it is probably identical with one of the other isomerides.

Nitromethoxycresol [Me : NO_2 : OMe = 1 : 2 : 4] solidifies at low temperatures, forming yellow prismatic crystals which melt at 17°. J. B. T.

Action of Nitrous Acid on some Unsaturated Aromatic Compounds. By A. Angeli (*Ber.*, **24**, 3994—3996).—Compounds, such as apiole, safrole, eugenol, and methyleugenol, which contain an allyl group are not acted on by nitrous acid; the corresponding isomerides, isoapiole, isosafrole, and isomethyleugenole and asaron, and anethoïl, compounds which contain the propenyl group, react readily with nitrous acid, yielding in every case two products, namely, the true nitrosite, and a compound differing therefrom in composition by 1 mol. H_2O.

Isosafrole nitrosite, $C_{10}H_{10}N_2O_5$, crystallises in colourless needles, and melts at 132°; the second product crystallises in yellow needles, melts at 124°, and has the composition $C_{10}H_8N_2O_4$.

The isapiole derivative, $C_{12}H_{12}N_2O_6$, melts at 170°; the methyliso-eugenol derivative melts at 117°. F. S. K.

Hexachloroparadiketohexene. By T. Zincke and O. Fuchs (*Annalen*, **267**, 1—47; compare Zincke, Abstr., 1890, 964).—Hexachloroparadiketohexene, $\begin{matrix}CCl{\cdot}CO{\cdot}CCl_2\\ \|\quad\quad\quad|\\ CCl{\cdot}CO{\cdot}CCl_2\end{matrix}$, is best prepared by heating

chloranil (5 grams) with manganese dioxide (5 grams) and hydrochloric acid of sp. gr. 1·19 (15 grams) at 180° for 10 hours. It melts at 89°, and boils at 275—285°, with partial decomposition into chlorine and chloranil; it is readily volatile with steam, and has a peculiar, irritating odour. On prolonged boiling with acetic acid, it is converted into chloranil, the same change taking place when it is heated with acetic acid and potassium iodide; when heated with dilute acetic acid at 140—150° for some hours, or when treated with stannous chloride, it is reduced to tetrachloroquinol. When shaken with 10 per cent. potash in the cold, it is decomposed into dichloromaleïc acid (m. p. 119—120°), trichlorethylene, and hydrogen chloride; well-cooled alcoholic potash converts it into an oily acid, which has probably the constitution $CCl_2{:}CCl{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COOH$, since it is decomposed into trichlorethylene and dichloromaleïc acid by aqueous alkalis.

Pentachloranilidoparadiketohexene (m. p. 144°) is moderately easily soluble in most of the ordinary solvents, except water, and is very stable towards concentrated hydrochloric acid. When its warm alcoholic solution is treated with stannous chloride until it becomes pale yellow, and the product is then oxidised with ferric chloride, trichloranilidoquinone is deposited in blue needles, together with some other substance, probably the corresponding dichloro-derivative.

αββ-Trichlorophenyl-*γ*-pyridonecarboxylic acid (m. p. 245°) crystallises in small, colourless needles, and is only sparingly soluble in ether, chloroform, and benzene, and almost insoluble in warm water. The *barium* salt, $(C_{12}H_5Cl_3NO_3)_2Ba$, is a crystalline compound readily soluble in warm water. The *silver* salt, $C_{12}H_5Cl_3NO_3Ag$, crystallises in colourless needles, is very sparingly soluble in cold water, and quickly turns violet on exposure to light. The *methyl* salt crystallises from hot alcohol in plates, and melts at 205° with decomposition.

αββ-Trichloro-γ-phenylpyridone, $\begin{matrix} CCl{\cdot}NPh{\cdot}CH \\ \| \qquad\quad \| \\ CCl{\cdot}CO{\cdot}CCl \end{matrix}$, is produced when the preceding compound is boiled with alcohol or acetic acid, or heated alone at its melting point. It crystallises from dilute alcohol in colourless needles, melts at 245°, and is readily soluble in hot glacial acetic acid, but more sparingly in hot alcohol, and almost insoluble in benzene, ether, and chloroform; it is not acted on by phenylhydrazine, aniline, hydroxylamine, or methyl iodide.

ββ-Dichloro-α-hydroxyphenylpyridonecarboxylic acid (m. p. 206°) crystallises in colourless needles, and is almost insoluble in benzene, chloroform, and light petroleum, but moderately easily in warm water, and readily in ether, alcohol, and glacial acetic acid; it is not acted on by phenylhydrazine, hydroxylamine, or aniline in alcoholic solution, but it is readily oxidised and destroyed by hot, dilute nitric acid. The *silver* salt, $C_{12}H_5Cl_2NO_4Ag_2$, is a colourless, crystalline compound, moderately stable in the light; it explodes when heated in a dry state. The *barium* salt is readily soluble. The *methyl* salt, $C_{14}H_{11}Cl_2NO_4$, prepared from the silver salt, crystallises from dilute alcohol in rhombic plates, melts at 140°, and dissolves freely in chloroform, benzene, alcohol, and glacial acetic acid, but is almost insoluble in ether and light petroleum, and insoluble in water.

Acetoxydichloropyridone, $C_{13}H_9Cl_2O_3N$, is obtained when dichlorohydroxypyridonecarboxylic acid is heated with acetic anhydride and sodium acetate until the evolution of carbonic anhydride ceases; it crystallises from acetic acid in colourless, nacreous plates, melts at 143°, and is readily soluble in warm alcohol, glacial acetic acid, benzene, and chloroform, and moderately easily in ether, but insoluble in water and light petroleum.

ββ-Dichloro-α-hydroxyphenylpyridone, $C_{11}H_7Cl_2NO_2$, can be obtained by heating the carboxy-derivative, described above, or by warming trichlorophenylpyridone with 10 per cent. alcoholic potash; it is, however, best prepared by hydrolysing acetoxydichlorophenylpyridone with 10 per cent. alcoholic soda. It crystallises from hot alcohol in colourless needles, melts at 192°, and is moderately easily soluble in alcohol, ether, chloroform, and hot water, but almost insoluble in benzene and light petroleum. The *sodium* derivative crystallises in colourless needles, and is readily soluble in water. The *barium* derivative crystallises in colourless, seemingly rhombic plates. The *silver* derivative crystallises in colourless needles, and is moderately stable in the light. The *methyl* derivative crystallises from dilute alcohol in yellowish needles melting at 136°.

Pentachloro-α-ketophenyl-γ-piperidone, $\begin{matrix}CO\cdot NPh\cdot CHCl\\ |\quad\quad\quad\quad |\\ CCl_2\cdot CO\cdot CCl_2\end{matrix}$, is deposited in crystals when chlorine is passed into a concentrated glacial acetic acid solution of dichlorohydroxyphenylpyridone; it crystallises in thin plates, melts at 147°, and is moderately easily soluble in benzene, light petroleum, chloroform, ether, hot glacial acetic acid, and hot alcohol, but insoluble in water. It liberates iodine from potassium iodide, and is readily decomposed by soda with formation of dichloracetanilide (m. p. 119°), aniline, and other products, the nature of which could not be determined. On reduction with stannous chloride in warm glacial acetic acid solution, it seems to yield a mixture of dichlorhydroxy- and tetrachlorhydroxy-phenylpyridone. When warmed with potassium acetate in acetic acid solution, 1 atom of chlorine is displaced by an acetyl group, a compound of the composition $C_{13}H_9Cl_4NO_4$ being formed; this substance crystallises from dilute acetic acid in slender needles, and melts at 150°.

An *acid* of the composition $C_{12}NH_{13}Cl_4O_5$ is formed when pentachloroketophenylpiperidone is gradually treated with 10 per cent. soda in cold methyl alcoholic solution; it separates from a mixture of ether and light petroleum in compact, transparent, seemingly rhombic crystals, melting at 114° with decomposition. It dissolves unchanged in soda, but on keeping the solution for a long time an odour of carbylamine is observed, and the solution then contains aniline and an oily acid which, from an analysis of its calcium salt, is probably dichloracetic acid. The constitution of the acid is probably represented by the formula

$$CHCl_2\cdot C(OH)_2\cdot NPh\cdot CH(OMe)\cdot CCl_2\cdot COOH.$$

Pentachloromethylamidoparadiketohexene, $\begin{matrix}CCl_2\cdot CO\cdot C\cdot NHMe\\ \|\quad\quad\quad\quad \|\\ CCl_2\cdot CO\cdot CCl\end{matrix}$, is

formed when an aqueous solution of methylamine is gradually added to an ethereal solution of hexachlorodiketohexene; it forms yellow needles, melts at 134°, and is readily soluble in alcohol, ether, and glacial acetic acid, but rather more sparingly in light petroleum and benzene, and insoluble in water.

αββ-Trichloromethyl-γ-pyridonecarboxylic acid, $\begin{matrix}CCl\cdot NMe\cdot C\cdot COOH\\ \|\quad\quad\quad\quad\|\\ CCl\cdot CO\cdot CCl\end{matrix}$, prepared by treating the preceding compound with 10 per cent. soda, crystallises from hydrochloric acid in slender, colourless needles, melts at 220°, with evolution of carbonic anhydride, and is decomposed on boiling with alcohol, glacial acetic acid, or water, yielding trichloromethylpyridone.

αββ-Trichloromethyl-γ-pyridone, $\begin{matrix}CCl\cdot NMe\cdot CH\\ \|\quad\quad\quad\|\\ CCl\cdot CO\cdot CCl\end{matrix}$, crystallises in slender, colourless needles, melts at 222°, and is readily soluble in water and ether.

A compound of the constitution $CCl_2{:}CCl\cdot CO\cdot CCl{:}CCl\cdot CO\cdot NHMe$ is formed when an aqueous solution of methylamine is gradually added to a well-cooled alcoholic solution of the hexachlorodiketone; it crystallises from boiling light petroleum in transparent plates, melts at 126°, and is readily soluble in most ordinary solvents except water. It dissolves unchanged in cold soda, but on heating the solution, complete decomposition ensues; when warmed with barium hydroxide, it is decomposed into dichloromaleïc acid, methylamine, and trichlorethylene.

Pentachloramidoparadiketohexene, $\begin{matrix}CCl_2\cdot CO\cdot C\cdot NH_2\\ \|\quad\quad\quad\|\\ CCl_2\cdot CO\cdot CCl\end{matrix}$, can be prepared by treating the hexachlorodiketone with anhydrous ammonia in well-cooled ethereal solution; it crystallises from water in yellow needles, melts at 141—142°, and dissolves freely in potash without evolution of ammonia. F. S. K.

Metachloroparacetotoluidide. By E. Lellmann (*Ber.*, **24**, 4111—4112).—The author criticises a recent paper of Erdmann's on this subject (Abstr., 1891, 1466). Metachloroparacetotoluidide is most conveniently prepared by dissolving paracetotoluidide (50 grams) in glacial acetic acid (400 grams), and treating the solution with chlorine diluted with 2 vols. of anhydrous carbonic anhydride; the product is separated from the acid, dried over quicklime, and recrystallised twice from dilute alcohol; it melts at 118°, and is quite pure. The yield is 40—42 per cent. of the theory, but it could probably be increased by the use of a larger proportion of acetic acid.

J. B. T.

Dimolecular Nitriles. By P. S. Burns (*J. pr. Chem.* [2], **44**, 568—570).—When benzoylimidopropionylethyl cyanide (Abstr., 1891, 888) is treated with phosphoric chloride, it yields a *chloro-derivative*, $N\leqslant^{CPhCl}_{CEt-}>CMe\cdot CN$, which melts at 97°; this points to the constitution $N\leqslant^{CPh(OH)}_{CEt-\!-\!-\!-}>CMe\cdot CN$ for the benzoyl derivative. When

the chlorinated derivative is heated with hydrochloric acid at 150°, it is reconverted into the benzoyl derivative; whilst heating with alcoholic potassium hydroxide gives rise to the corresponding *ethoxy-derivative*, melting at 55°.

The reaction between imidopropionylmethyl cyanide and benzoic chloride (2 mol. proportions) yields a *compound*, NBz:CMe·CHBz·CN, which forms beautiful crystals melting at 158°. Alcoholic potassium hydroxide converts this into *acetylbenzoylmethyl cyanide* (*α-cyanobenzoylacetone*), COMe·CHBz·CN, which crystallises in prisms, melts at 74°, and is decomposed by water at 150° into benzoylacetone, carbonic anhydride, and ammonia. Acetylbenzoylmethyl cyanide has the properties of a *β*-diketone; with ammonia, it yields an *imido-derivative*, which crystallises in needles melting at 148°, and with phenylhydrazine, a *compound*, $C_{17}H_{13}N_3$, which melts at 189°, and is probably cyanodiphenylmethylpyrazolone. A. G. B.

Substitution of the Azo-Group for Ketonic Oxygen. By T. Curtius and H. Lang (*J. pr. Chem.* [2], **44**, 544—568; compare Abstr., 1889, 1157; 1891, 39).—Benzoylphenylazomethylene (Abstr., 1891, 1357) explodes when sharply heated above its melting point; it dissolves easily in alcohol, less so in ether and benzene, and not at all in water. When it is treated with iodine (1 mol. proportion) in alcoholic solution, nitrogen is evolved, and *benzoylphenyldiiodomethane* (diiododeoxybenzoïn) separates as a colourless, crystalline powder, which was not analysed; it is decomposed by air into benzile and hydrogen iodide. By the action of bromine on a chloroform solution of benzoylphenylazomethylene, benzoylphenyldibromomethane (dibromodeoxybenzoïn), melting at 112°, is formed; the same compound obtained by the action of bromine on deoxybenzoïn melts at 110—112° (*Annalen*, **155**, 68); when heated with water, it is decomposed into benzile and hydrogen bromide; silver nitrate removes all its bromine in the cold.

By the action of hydrogen chloride on an ethereal solution of benzoylphenylazomethylene, chlorodeoxybenzoïn and nitrogen are formed. *Chlorodeoxybenzoïn* crystallises in long, colourless needles, and melts at 65°; the chlorodeoxybenzoïn prepared from dichlorodeoxybenzoïn is described in *Ber.*, **17**, 1163, as a thick, yellow oil crystallising below 0°. With zinc-dust and glacial acetic acid in ether, benzoylphenylazomethylene is reduced to deoxybenzoïn (m. p. 55°; b. p. 310°) with formation of ammonia. With hot water, benzoylphenylazomethylene yields, among other substances, a colourless compound which melts at 151°; with hot, dilute sulphuric acid or potassium hydroxide, it explodes; with hot alcohol, a sparingly soluble substance separates in greenish needles, melting at 192°. When benzoylphenylazomethylene decomposes spontaneously, it becomes converted into an opaque, white substance, which is free from nitrogen, but has not been otherwise analysed.

Azoisatin, $N\lessdot^{C(OH)}_{C_6H_4-}\!\!>C{:}N_2$, is obtained as its mercury compound when hydrazisatin (10 grams. Abstr., 1891, 1360) is heated with mercuric oxide (20 grams) and benzene (500 grams) for several days

in a reflux apparatus; the liquid is filtered while hot, and the residue washed with benzene, and extracted with hot alcohol; the alcoholic solution is then evaporated, and the residual mercury compound suspended in water through which hydrogen sulphide is passed; when all the mercury is separated, the azoisatin is extracted with ether. Azoisatin crystallises from benzene or glacial acetic acid in small, dark-red prisms; it melts with evolution of gas at 161°, and explodes when sharply heated, with the production of brown fumes; it is easily soluble in benzene, chloroform, and glacial acetic acid, but less so in ether, and still less so in cold absolute alcohol; it is not changed by hot water, and only with difficulty attacked by alcoholic solution of iodine; mineral acids decompose it in the cold. Determinations of the molecular weight of azoisatin by the cryoscopic method indicate that the above formula should be doubled; the constitution of the substance is thus a little uncertain. The *mercury compound*, $(C_8H_4N_3O)_2Hg$, crystallises in microscopic, dark-brown needles, which are stable in air, and explode when heated.

Diammonium methylhydrazimethylenecarboxylate,

$$N_2H_2{:}CMe{\cdot}COOH,N_2H_4$$

(compare Abstr., 1891, 39), is obtained when pyruvic acid is neutralised with hydrazine hydrate in alcoholic solution, another molecular proportion of hydrazine hydrate added, the mixture warmed for a short time on the water-bath, and slowly evaporated; it forms a colourless, crystalline powder, melts at 115—117°, and is moderately soluble in water. With benzaldehyde, it yields benzalazine. When barium pyruvate and hydrazine sulphate, in molecular proportion, are ground together with water, the mixture becomes warm, and neither barium nor sulphuric acid can be detected in the filtrate; but when it is evaporated to a syrup and mixed with absolute alcohol, an oil separates and gradually solidifies to a white, crystalline, hygroscopic mass, $C_5H_{10}N_2O_3$, which melts at 121°.

Methyl hydrazopropionate has been already described (Abstr., 1891, 39).

Ethyl hydrazopropionate, $N_2H_2{:}CMe{\cdot}COOEt$, is left in solution when the product of the action of ethyl pyroracemate on hydrazine hydrate (in molecular proportion) is crystallised from alcohol, and is obtained in colourless needles by evaporating this mother liquor. The laminæ, which are less soluble in alcohol, are *hydrazopropionylhydrazine*, $N_2H_2{:}CMe{\cdot}CO{\cdot}NH{\cdot}NH_2$, which forms a white, crystalline compound when shaken with benzaldehyde in aqueous solution; no such condensation product is obtained from ethyl hydrazopropionate—an indication that the latter contains the group NHNH, and not NNH_2.

Methyl azomethylenecarboxylate (methyl α-diazopropionate),

$$N_2{:}CMe{\cdot}COOMe,$$

is obtained by the action of mercuric oxide on methyl hydrazopropionate in benzene; it cannot be separated from the benzene by fractional distillation, as it does not distil without decomposition. When the benzene solution is acted on by iodine and ammonia, *α-diiodopropionamide*, $Me{\cdot}CI_2{\cdot}CONH_2$, is formed; it crystallises in small, yellow needles, and melts at 127°, but has not been analysed.

Methyl α-amidopropionate hydrochloride, $NH_2{\cdot}CHMe{\cdot}COOMe,HCl$, obtained by the action of methyl alcohol and hydrogen chloride on α-alanine, crystallises in colourless, slender prisms, and melts at 157°; it deliquesces with water, and is soluble in hot alcohol, but not in ether and benzene. By diazotising 50 grams of this compound, and distilling under reduced pressure, 4 grams of methyl azomethylenecarboxylic acid were obtained.

From the above experiments, it may be generally stated that by the successive action of hydrazine and mercuric oxide on α-ketonic acids, the ketonic oxygen can be displaced by the azo-group, the same compounds being produced as are obtained by the action of nitrous acid on the ethereal salts of amido-aliphatic acids.

Diethyl aspartate (Abstr., 1885, 885; *J. pr. Chem.* [2], **38**, 474), explodes when heated to 150° under 12 mm. pressure; it yields *asymmetrical diiodosuccinamide* when treated with iodine and concentrated ammonia; this crystallises in nearly colourless, lustrous tables.

Methyl diazoacetate boils at 73° under 80 mm. pressure; ethyl diazoacetate boils at 84° under 61 mm. pressure; amyl diazoacetate boils at 89° under 13 mm. pressure.

Ethyl azimethylenedicarboxylate, $COOEt{\cdot}CH{:}N_2{:}CH{\cdot}COOEt$, is the residue (4 per cent.) left on fractionating ethyl diazoacetate; it is a yellow liquid which smells of cyanogen and hydrocyanic acid; it boils at 42° (12 mm.), and is insoluble in water; when evaporated with acid silver nitrate, it yields silver cyanide, and when hydrolysed by acids or alkalis, it yields acetic acid and hydrazine. This salt is a powerful reducing agent, and yields benzalazine with alkaline benzaldehyde.

Diammonium phenylhydrazimethylenecarboxylate,

$$N_2H_2{:}CPh{\cdot}COOH,N_2H_4,$$

is obtained by acting on well-cooled ethyl benzoylformate with hydrazine hydrate (1 mol. proportion) in alcohol; it forms colourless, spherical crystals, and melts at 118—120°; it is a strong reducing agent, dissolves sparingly in cold, and freely in hot, water, and yields benzalazine with benzaldehyde. When less than one molecular proportion of hydrazine hydrate was used, a substance which was probably *diethyl diphenylazimethylenedicarboxylate*,

$$COOEt{\cdot}CPh{:}N{\cdot}N{:}CPh{\cdot}COOEt,$$

was obtained; this crystallises in yellow needles, melts at 135°, and is freely soluble in hot alcohol and ether; it is very stable towards cold acids and alkalis; when it is warmed with concentrated sulphuric acid and water added, an aromatic oil and hydrazine sulphate are produced; when gradually heated, it sublimes unchanged, but is decomposed by rapid heating. A. G. B.

Derivatives of Phenylhydrazine. By C. Willgerodt and E. G. Mühe (*J. pr. Chem.* [2], **44**, 451—466).—*Metachlorophenylhydrazine*, $C_6H_4Cl{\cdot}NH{\cdot}NH_2$ [Cl : NH·NH$_2$ = 3 : 1], obtained by the reduction of metachlorodiazobenzene with stannous chloride, is a brownish-red

oil, insoluble in water, but soluble in alcohol, toluene, ether, and chloroform. The *hydrochloride* crystallises in white laminæ, melts at 235—236°, and dissolves in hot water, hot alcohol, slightly in ether and hot chloroform, not at all in benzene.

Picrylmetachlorophenylhydrazine, $C_6H_2(NO_2)_3{\cdot}NH{\cdot}NH{\cdot}C_6H_4Cl$, prepared from metachlorophenylhydrazine and picryl chloride, crystallises in small, red prisms, decomposes at 177—178°, and dissolves in glacial acetic acid, benzene, hot ether, chloroform, but only sparingly in alcohol, and not at all in water.

Picrylmetachlorazobenzene, $C_6H_2(NO_2)_3{\cdot}N_2{\cdot}C_6H_4Cl$, obtained by oxidising picrylmetachlorophenylhydrazine, crystallises in red laminæ, melts at 138—139°, and dissolves in glacial acetic acid, alcohol, benzene, and chloroform, but not in water.

Dinitronitrosophenylmetachlorazobenzene, $NO{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_6H_4Cl$, prepared by heating picrylmetachlorophenylhydrazine with glacial acetic acid in a reflux apparatus, crystallises in yellow prisms or laminæ, melts at 204—205°, and dissolves easily in glacial acetic acid, benzene, and chloroform, sparingly in alcohol, and not at all in water.

Dinitrosonitrophenylmetachlorazobenzene, $NO_2{\cdot}C_6H_2(NO)_2{\cdot}N_2{\cdot}C_6H_4Cl$, prepared by heating picrylmetachlorophenylhydrazine with alcohol at 120°, crystallises in yellow laminæ, melts at 184° (uncorr.), and dissolves in glacial acetic acid, benzene, and chloroform, but not in water.

Dinitronitrosophenylnitrometachlorazobenzene,

$$NO{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_6H_3Cl{\cdot}NO_2,$$

obtained in the nitration of dinitronitrosometachlorazobenzene, is a yellow, amorphous powder, decomposes at 194°, and dissolves easily in glacial acetic acid and chloroform, but only sparingly in hot alcohol and ether.

Picrylnitrometachlorazobenzene, $C_6H_2(NO_2)_3{\cdot}N_2{\cdot}C_6H_3Cl{\cdot}NO_2$, from the nitration of picrylmetachlorazobenzene, crystallises in yellow laminæ, decomposes at 124—125°, and is freely soluble in glacial acetic acid, benzene, and toluene, but only sparingly in alcohol, ether, and chloroform.

Orthoparadinitrophenylmetachlorophenylhydrazine,

$$C_6H_3(NO_2)_2{\cdot}N_2H_2{\cdot}C_6H_4Cl,$$

is obtained by heating alcoholic solutions of α-dinitrochlorobenzene (1 mol.) and metachlorophenylhydrazine (2 mols.) together in a reflux apparatus; it crystallises in beautiful, yellow, rhombic prisms, melts at 151—152°, and dissolves in glacial acetic acid, alcohol, benzene, and chloroform.

α-Dinitrophenylmetachlorazobenzene, $C_6H_3(NO_2)_2{\cdot}N_2{\cdot}C_6H_4Cl$, from the oxidation of the preceding compound, crystallises in slender, red needles, and melts at 122—123°; it dissolves in glacial acetic acid, chloroform, and alcohol.

Nitronitrosophenylmetachlorazobenzene, $NO_2{\cdot}C_6H_3(NO){\cdot}N_2{\cdot}C_6H_4Cl$, obtained by the prolonged heating of the corresponding hydrazine with glacial acetic acid, crystallises in yellow, slender needles; it melts at 202°, and is sparingly soluble in alcohol, but freely in glacial acetic acid.

Orthoparadinitrosophenylmetachlorazobenzene, $C_6H_3(NO)_2 \cdot N_2 \cdot C_6H_4Cl$, is prepared from orthoparadinitrophenylmetachlorophenylhydrazine by heating it with alcohol in a sealed tube at 150° for six hours; it crystallises in soft, white needles, melts at 159°, and is only sparingly soluble in alcohol, but easily so in glacial acetic acid, benzene, and chloroform.

Orthoparadinitrophenylnitrometachlorazobenzene,

$$C_6H_3(NO_2)_2 \cdot N_2 \cdot C\,H_3Cl \cdot NO_2,$$

from the nitration of the dinitrometachlorazobenzene, crystallises in yellowish-red needles, decomposes at 165°, and is sparingly soluble in alcohol, although freely in glacial acetic acid, chloroform, and benzene.

Nitronitrosophenylmetachlorazoxybenzene,

$$NO \cdot C_6H_3(NO_2) \cdot N_2O \cdot C_6H_4Cl,$$

obtained by oxidising the nitronitrosophenylmetachlorazobenzene with chromic acid in glacial acetic acid, crystallises in slender, yellow needles which melt at 166—167°; it dissolves in glacial acetic acid, benzene, and chloroform, but only sparingly in ether.

Trinitronitrosoazobenzenephenylhydrazine,

$$N_2H_2Ph \cdot C_6H_3(NO_2) \cdot N_2 \cdot C_6H_2(NO_2)_2 \cdot NO,$$

prepared from trinitronitrosometachlorazobenzene and phenylhydrazine, is an amorphous, red powder, decomposes at 130°, and is soluble in alcohol, chloroform, and glacial acetic acid.

Dinitrodinitrosodisazobenzene, $NO \cdot C_6H_2(NO_2)_2 \cdot N_2 \cdot C_6H_3(NO) \cdot N_2Ph$, obtained by heating the preceding compound with alcohol, is a yellowish-brown, amorphous substance; it decomposes at 158°, and is easily soluble in chloroform and glacial acetic acid.

Nitrotrinitrosodisazobenzene, $NO_2 \cdot C_6H_2(NO)_2 \cdot N_2 \cdot C_6H_3(NO) \cdot N_2Ph$, obtained by heating trinitronitrosoazobenzenephenylhydrazine with alcohol in a sealed tube for three hours at 160°, is an amorphous, brown substance, melts at 175—176° with decomposition, and dissolves sparingly in alcohol, but more freely in glacial acetic acid and chloroform.

Trinitronitrosoazobenzenemetachlorophenylhydrazine,

$$NO \cdot C_6H_2(NO_2)_2 \cdot N_2 \cdot C_6H_3(NO_2) \cdot N_2H_2 \cdot C_6H_4Cl,$$

prepared from trinitronitrosometachlorazobenzene and metachlorophenylhydrazine, is a yellow-brown, amorphous substance, decomposes at 169—170°, and dissolves sparingly in alcohol, but more easily in chloroform, benzene, and glacial acetic acid.

Tetranitrazobenzenephenylhydrazine,

$$C_6H_2(NO_2)_3 \cdot N_2 \cdot C_6H_3(NO_2) \cdot N_2H_2Ph,$$

obtained from tetranitrometachlorazobenzene and phenylhydrazine, is a reddish-brown, amorphous substance, decomposes at 193°, and is sparingly soluble in alcohol, but more freely in benzene and glacial acetic acid.

Tetranitrazobenzenemetachlorophenylhydrazine,

$$C_6H_2(NO_2)_3 \cdot N_2 \cdot C_6H_3(NO_2) \cdot N_2H_2 \cdot C_6H_4Cl,$$

is dark-brown and amorphous; it blackens at 160—170°, and decomposes at 205—206°; it dissolves in benzene, toluene, chloroform, and glacial acetic acid.

Tetranitrometachlorodisazobenzene,

$$C_6H_2(NO_2)_3\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_4Cl,$$

obtained as described for the analogous compounds, crystallises in dark-red prisms, melts at 91°, and dissolves easily in organic solvents.

Dinitrodinitrosometachlorodisazobenzene,

$$NO\cdot C_6H_2(NO_2)_2\cdot N_2\cdot C_6H_3(NO)\cdot N_2\cdot C_6H_4Cl,$$

is a greenish-yellow, amorphous powder, decomposes at 225—226°, and is sparingly soluble in alcohol, but more freely in chloroform and benzene.

Pentanitrometachlorodisazobenzene,

$$C_6H_2(NO_2)_3\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_3Cl\cdot NO_2,$$

from the nitration of the corresponding tetranitro-compound, forms ill-defined, yellow crystals which decompose at 157°; it is moderately soluble in glacial acetic acid, benzene, and chloroform, but only sparingly in alcohol.

Trinitrazobenzenemetachlorophenylhydrazine,

$$C_6H_3(NO_2)_2\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2H_2\cdot C_6H_4Cl,$$

prepared from trinitrometachlorazobenzene and metachlorophenylhydrazine, is a yellowish-brown, amorphous substance, decomposes at 127—128°, and dissolves in benzene and chloroform, but hardly at all in alcohol.

Pentanitrodisazobenzenephenylhydrazine,

$$C_6H_2(NO_2)_3\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2H_2Ph,$$

is a dark, red-brown, amorphous substance; it decomposes at 144°, and dissolves sparingly in alcohol, but better in benzene, chloroform, and glacial acetic acid. A. G. B.

Secondary Asymmetrical Hydrazines obtained by the Action of Aldehydes or Ketones on Hydrazine Hydrate. By T. Curtius and L. Pflug (*J. pr. Chem.* [2], **44**, 535—544; compare Abstr., 1889, 393; 1891, 1355—1360).—As already pointed out (Abstr., 1891, 1355), when hydrazine hydrate (1 mol. proportion) acts on an aldehyde or ketone (2 mol. proportions), di- and tetra-substitution products of azimethylene are respectively produced. When, however, an aldehyde or ketone is added to an excess of hydrazine hydrate, asymmetrical secondary hydrazines are produced. These are, with few exceptions, unstable bases, readily decomposing into hydrazine and azimethylene derivatives.

Benzalhydrazine (phenylmethylenehydrazine), $CHPh{:}N\cdot NH_2$, was described as cinnamalbenzalazine by Curtius and Thun (Abstr., 1891, 1357). It can be obtained pure as follows:—10 grams of hydrazine hydrate is placed in a flask with some barium oxide, and 19 grams of benzaldehyde is gradually added with constant shaking. After several hours' digestion on the water-bath, 2 volumes of dry

ether are added to the cooled flask, and the mixture filtered; the ethereal solution is dried for several days over potassium hydroxide, filtered, and distilled under a pressure of 14 mm., when benzalhydrazine distils over in almost the calculated quantity at 140°. Benzalhydrazine is a clear, colourless liquid, boils at 140° (14 mm.), and solidifies at 12° to a white mass of tabular crystals which melt at 16°; it has an intense odour of hot soap-lye, reduces alcoholic ammoniacal silver solution, and must be preserved in a sealed tube, as it decomposes very rapidly in moist air with formation of benzalazine and hydrazine hydrate.

Benzaldehyde reacts with benzalhydrazine to form benzalazine and water; iodine reacts with it to form benzalazine, nitrogen, and hydrogen iodide, which reacts with more benzalhydrazine, forming benzalazine and diammonium iodide (hydrazine monohydriodide, m. p. 125°; compare Abstr., 1891, 264). When reduced by sodium amalgam in ether, benzalhydrazine yields benzalazine, and, on addition of hydrochloric acid to the ethereal liquid, diammonium dichloride (m. p. 197°; compare Abstr., 1889, 340) crystallises out; hydrogen chloride passed into a dry ethereal solution of benzalhydrazine brings about the same change.

When a solution of benzalhydrazine in benzene is treated with mercuric oxide in the cold, it becomes of a deep, carmine colour. This indicates the formation of a benzaltetrazone, analogous to diphenylmethylenetetrazone (Abstr., 1891, 1359), but the colour of the solution rapidly fades, with evolution of nitrogen and formation of benzalazine.

Phenylmethylmethylenehydrazine, $CMePh{:}N{\cdot}NH_2$, is prepared by digesting a mixture of acetophenone (10 grams) with hydrazine hydrate (8 grams) and some sticks of barium oxide for three days on the water-bath, then adding more barium oxide and 5 volumes of absolute ether; the filtrate is fractionated, most of it distilling between 240° and 260°; this portion is the new hydrazine, the residue in the retort being bimethylphenylazimethylene (Abstr., 1891, 1355). Phenylmethylmethylenehydrazine is a pale-yellow liquid, boils at 255°, and is extremely unstable in moist air; even in absence of air it gradually loses nitrogen and ammonia, yielding dimethylphenylazimethylene. With mercuric oxide, it becomes deep-red, but the tetrazone is very unstable.

Phenylmethylphenylazimethylene, $CMePh{:}N{\cdot}N{:}CHPh$, is obtained by shaking phenylmethylmethylenehydrazine with benzaldehyde and water rendered feebly alkaline and crystallising the product from alcohol; it forms yellow, spear-shaped prisms, melts at 59°, and dissolves easily in ether, benzene, and alcohol, but not in water.

When methyl propyl ketone (15 grams) and hydrazine hydrate (10 grams) are heated with barium oxide, the product of the action distils between 160° and 170°, and behaves as methylpropylmethylenehydrazine, but, on redistillation, it evolves gas and becomes dimethylpropylazimethylene (Abstr., 1891, 1355).

Dimethylmethylenehydrazine, $CMe_2{:}N{\cdot}NH_2$, is prepared by gradually adding acetone (15 grams) to a mixture of hydrazine hydrate (15 grams) with barium oxide; after seven days, the impure base (17·5 grams) may be poured off and distilled. This compound is a

clear, colourless, mobile liquid, boils at 124—125°, and decomposes, when kept, with evolution of nitrogen and ammonia; with benzaldehyde, it yields acetone and benzalazine. It is coloured intensely red by mercuric oxide. A. G. B.

Action of Phenylhydrazine on Ethyl Ethoxyoxalacetate. By W. Wislicenus and M. Scheidt (*Ber.*, **24**, 4210—4214; compare this vol., p. 49).—When phenylhydrazine is added to a cold aqueous solution of ethyl ethoxyoxalacetate, an *additive* compound separates as a yellow oil which subsequently solidifies; it crystallises from alcohol in small, white crystals, melts at 111°, has the composition $C_{16}H_{24}N_2O_6$, and is insoluble in cold ether, sparingly soluble in cold water and alcohol, readily so in the boiling liquids; phenylhydrazine separates on treating it with cold aqueous alkalis.

Ethyl ethoxyoxalacetate phenylhydrazone,

$$COOEt\cdot C(N_2HPh)\cdot CH(OEt)\cdot COOEt,$$

is obtained by heating the last-described compound with alcohol and adding water, when an oil separates which solidifies after a while, and is purified by dissolving in alcohol, adding water until turbidity is produced, and filtering from resin; it separates, on allowing the filtrate to remain, in long, yellow needles, melts at 52—54°, and is soluble in all solvents, except water.

Ethyl phenylhydrazoneketophenylpyrazolonecarboxylate,

$$NPh\begin{cases} N=C\cdot COOEt \\ CO\cdot C:N_2HPh \end{cases},$$

is produced by boiling an acetic acid solution of ethyl ethoxyoxalacetate (1 mol.) and phenylhydrazine (3 mols.) in a reflux apparatus for an hour, pouring into water, extracting the precipitated oil with ether, washing the ethereal solution with alkali, and, after removing the solvent, crystallising from alcohol and light petroleum; it forms small, orange-yellow needles, melts at 152—154°, and is sparingly soluble in water, and not very readily so in ether. The corresponding acid, which is identical with that of Knorr (Abstr., 1888, 724), is obtained by treating the ethyl salt with aqueous potassium hydroxide. A. R. L.

Action of Acetic Anhydride on Diazoamido-compounds. By F. Heusler (*Ber.*, **24**, 4156—4161).—Diazoamidobenzene reacts with explosive violence when warmed with acetic anhydride, but the reaction proceeds with tranquillity if the reagents are heated together in the presence of dry toluene, nitrogen being evolved, and a small quantity of an oil, having the odour and boiling point of diphenyl ether, together with acetanilide, being obtained.

Benzenediazoacetanilide, $PhN_2\cdot NPhAc$, is produced when diazoamidobenzene (100 grams) is shaken with acetic anhydride (60 grams) and absolute ether (300 grams) and the mixture allowed to remain in a closed flask for five weeks at the temperature of the room. At the end of this time, needles separate and adhere to the sides of the flask; these are dissolved in chloroform, and the compound precipitated

by the addition of ether; it melts at 129—130° with decomposition, deflagrates when heated to a high temperature, and decomposes into phenol, acetic acid, aniline, and nitrogen, on boiling with dilute mineral acids; it also decomposes, when heated with ethyl alcohol, giving rise to benzene, aldehyde, acetanilide, and nitrogen, but attempts to separate diazobenzene ethyl ether, which is perhaps formed in the first stage of the decomposition, were unsuccessful. A similar decomposition is occasioned, although not so readily, by other alcohols, but the formation of aldehydes was not observed. Benzenediazoacetanilide dissolves in alcoholic soda with the formation of diazoamidobenzene.

Toluenediazoacetotoluide, $Me^{1}\cdot C_6H_4^{4}\cdot N_2\cdot NAc\cdot C_6H_4^{1}Me$, is obtained from paradiazoamidotoluene and acetic anhydride in the same manner as the benzene derivative. The ethereal solution is shaken with dilute soda solution to free it from acid, and the compound isolated by evaporating the solvent; after repeated recrystallisation from ether, it forms colourless needles and melts at 104—105° with decomposition; it is very soluble in the usual organic solvents, and in its chemical behaviour resembles benzenediazoacetanilide.

Orthodiazoamidotoluene (see B. Fischer and Wimmer, Abstr., 1887, 819) is prepared by mixing orthotoluidine (2 mols.) dissolved in ether with amyl nitrite (1 mol.) in a dish at −20°, and, after allowing the mixture to remain for several hours, breaking up the crystalline cake, collecting, and washing the product first with 90 per cent. and then with more dilute alcohol; it melts at 51°. When orthodiazoamidotoluene is dissolved in benzene or ether and the mixture boiled in a reflux apparatus with acetic anhydride, and after distilling off the solvent, acidified with hydrochloric acid, boiled to hydrolyse the acetotoluide, steam distilled, then made alkaline and again steam distilled, a resinous mass remains, which, on purification, is found to be indazole. To avoid collision with the work of Witt, Nölting, and Grandmougin, who obtained nitroindazole from paranitrorthodiazotoluene (Abstr., 1891, 312), the author has relinquished the study of the action of acetic anhydride on compounds containing the diazo-group in the ortho-position relatively to the methyl radicle. He is at present engaged in studying the reaction between benzenediazopiperidide and acetic anhydride, and he states that no diphenyl ether is formed in this reaction. A. R. L.

Heat Developed in the Isomeric Change of the Oxime of Opianic Anhydride. By C. Liebermann (*Ber.*, **25**, 89—90).—The author, in conjunction with F. Stohmann, has determined the amount of heat developed in the change of the oxime of opianic anhydride to hemipinimide. The heat of combustion of the oxime of opianic anhydride was found to be 1152·3 Cal., that of hemipinimide 1099·7 Cal., giving a difference of 52·6 Cal. as the heat evolved by the molecular change. This amount of heat is 10 times that developed in the change of allocinnamic into cinnamic acid, and more than six times the amount due to the change of maleïc into fumaric acid.

E. C. R.

Action of Benzenesulphonic Chloride on Amidoximes. By F. Tiemann (*Ber.*, 24, 4162—4167).—The author makes general and introductory remarks on Pinnow's paper (next abstract).

A. R. L.

Action of Benzenesulphonic Chloride on Amidoximes. By J. Pinnow (*Ber.*, 24, 4167—4176).—Paramethylbenzenylamidoxime is converted into the isomeric paratolylcarbamide as follows:—The amidoxime (15 parts), mixed with finely powdered anhydrous sodium carbonate (5·3 parts), is suspended in chloroform (80 parts), and a solution of benzenesulphonic chloride (17·65 parts) in chloroform (40 parts) gradually added; carbonic anhydride is evolved with the development of heat, and the reaction is completed by heating the mixture on the water-bath for an hour; on now distilling off the solvent, and extracting the oily residue with boiling water, a white substance is obtained, which, after recrystallisation from a mixture of benzene and alcohol, melts at 180°, and has all the properties of paratolylcarbamide. The reaction probably occurs in two stages, thus:— $C_6H_4Me{\cdot}C(NONa){\cdot}NH_2 + PhSO_2Cl = C_6H_4Me{\cdot}N(OSO_2Ph){\cdot}NH_2 + NaCl$; and $C_6H_4Me{\cdot}N(OSO_2Ph){\cdot}NH_2 + H_2O = C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}NH_2 + PhSO_3H$.

Metabromoparatolylcarbamide, $C_6H_3MeBr{\cdot}NH{\cdot}CO{\cdot}NH_2$, is obtained, together with other bromo-derivatives, when paratolylcarbamide is dissolved in glacial acetic acid and treated with bromine; it is isolated by fractional crystallisation, melts at 184·5° (uncorr.), is insoluble in water, easily soluble in alcohol and benzene, and sparingly so in light petroleum; it yields metabromoparatoluidine (b. p. 240°), when heated with hydrochloric acid in a sealed tube at 160°, and gives benzonitrile and benzoylmetabromoparatoluidide (m. p. 148·5°) on heating it with benzoic chloride.

Benzenylamidoxime is coverted into phenylcarbamide by treating it with benzenesulphonic chloride in the above-described manner; the product of this reaction has been erroneously described as dehydrodibenzenylamidoxime by Goldberg (*Inaug. Diss., Berlin*, 1891); the triacetyldehydrodibenzenylamidoxime described by this author is acetylphenylcarbamide (Creath, this Journal, 1876, i, 400; Kühn, Abstr., 1885, 260); whilst the compound described as cyaphenine is diphenylcarbamide. Goldberg (*loc. cit.*) states that when the so-called dehydrodibenzenylamidoxime is brominated in glacial acetic acid solution, it yields a tribromo-derivative melting at 198°; in reality it is found that when phenylcarbamide is treated in this manner, a mixture of compounds results, from which *parabromophenylcarbamide*, $C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}NH_2$, a compound crystallising from benzene in white needles of a silvery lustre, and melting at 260°, may be isolated; the latter decomposes into parabromaniline, ammonia, and carbonic anhydride when heated in a sealed tube at 160°, and yields carbonic anhydride, benzonitrile, and *benzoylparabromanilide*, melting at 201°, on treatment with benzoic chloride.

The oil which remains after extracting the product of the reaction between paramethylbenzenylamidoxime and benzenesulphonic chloride (see above) with water yields on subsequent extraction with alcohol a

compound, probably $C_6H_4Me\cdot C<^{N\cdot O}_{N:SPhO}$, which forms silky needles, melts at 89°, and is indifferent towards acids and alkalis; a similar derivative, melting at 157—158°, is obtained from benzenylamidoxime. When a solution of phenylethenylamidoxime in chloroform is heated with anhydrous sodium carbonate and benzenesulphonic chloride, benzylcarbamide (m. p. 148°), together with a large quantity of *phenylethenylamidoximebenzenesulphone*, $CH_2Ph\cdot C(NH_2):NO\cdot SO_2Ph$, a compound sparingly soluble in water and easily so in boiling alcohol, crystallising therefrom in compact, lustrous crystals; it is, doubtless, the primary product of the reaction. A. R. L.

New Method of Preparing Benzenylhydrazoximamidobenzylidene. By F. Tiemann (*Ber.*, **24**, 4176—4177; compare Stieglitz, Abstr., 1890, 254).—When bromine is dropped into a solution of benzenylamidoxime in absolute alcohol, it is absorbed with the evolution of hydrogen bromide; after a while, however, the colour of the bromine no longer disappears, and later, a white, crystalline compound, and subsequently a red one separate; the former may be converted into the latter by treating it with bromine. These derivatives are so unstable that their composition could not be determined. When either is treated with aqueous ammonia, and the resulting white crystalline mass dissolved in alcohol, benzenylhydrazoximidobenzylidene separates on adding water; whilst dibenzenylazoxime is produced if the compounds are boiled with alcohol. A. R. L.

Constitution of the Hydroxamic Acids. By W. Lossen (*Ber.*, **24**, 4059—4062).—A reply to Tiemann (this vol., p. 300), in which the author upholds the general formula $R\cdot C(OH):NOH$ against that proposed by Tiemann (*loc. cit.*). A. R. L.

Constitution of the Hydroxamic Acids. By F. Tiemann (*Ber.*, **24**, 4062—4064).—A rejoinder to Lossen (preceding abstract).

Stereoisomeric Derivatives of Benzhydroxamic Acid. By A. Werner (*Ber.*, **25**, 27—48).—The nature of the hydroxamic acids has been frequently investigated and discussed; according to Lossen (Abstr., 1889, 1064), they have a constitution represented by the formula $R\cdot C(OH):N\cdot OH$, whilst Tiemann (this vol., p. 300) regards the tautomeric formula $R\cdot CO\cdot NH\cdot OH$ as more probable. There are also a number of derivatives of benzhydroxamic acid possessing, undoubtedly, the same structure, which, nevertheless, exist in two or more isomeric forms; for this fact no explanation has hitherto been given, although Lossen suggests that they may possibly be stereoisomerides. The author has, therefore, investigated the matter afresh, and finds that these compounds are, in reality, stereometric nitrogen isomerides.

The nomenclature of the hydroxamic acid derivatives is, at present, very confusing, and to simplify it the author makes the following alterations: the term *hydroxamic acid* is reserved for true hydroxy-derivatives of acid amides $R\cdot CO\cdot NH\cdot OH$ [or the tautomeric form $R\cdot C(OH):N\cdot OH$]. The compounds obtained from these by substitu-

tion of an alkyl or acidyl group for the labile hydrogen atom, and which can only exist in the "oxime" form $R{\cdot}C(OR'){:}N{\cdot}OH$, are termed *hydroximic acids*. The hydroxamic acids and their derivatives may be represented by the four following formulæ:—

(1.) $R{\cdot}CO{\cdot}NH{\cdot}OH$. (3.) $R{\cdot}CO{\cdot}NR''{\cdot}OH$.
(2.) $R{\cdot}CO{\cdot}NH{\cdot}OR'$. (4.) $R{\cdot}CO{\cdot}NH{\cdot}OR''$.

The compounds represented in formula (1) are the simple hydroxamic acids, and can also react in the tautomeric form $R{\cdot}C(OH){:}N{\cdot}OH$; their names are derived from that of the acidyl group they contain, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}OH$ being benzhydroxamic acid, as hitherto. The compounds of formula (2), that is, those in which the "acid" hydrogen atom is replaced by an alkyl or acidyl group, can also react in the tautomeric form, and are named in the usual manner according to the name of the substituent radicle. The compounds whose structure is represented by formulæ (3) and (4) do not show tautomerism, and are likewise named in the usual manner from the names of the radicles they contain. The hydroximic acids are represented by the general formulæ

(1.) $R{\cdot}C(OR'){:}N{\cdot}OH$, (2.) $R{\cdot}C(OR'){:}N{\cdot}OR''$.

The first represents the simple hydroximic acids, and the second their ethers or ethereal salts, according as R″ is an alkyl or acidyl group. A table of the more important benzhydroxamic acid derivatives with both their old and new names may be found in the original.

Ethylbenzhydroximic acid, $OEt{\cdot}CPh{:}N{\cdot}OH$, has been found by Lossen and his pupils to exist in two modifications (α- and β-). To ascertain that these have a distinct chemical individuality both were converted into the acetyl and paranitrobenzyl derivatives, which were found to be quite distinct compounds in both cases; the identity of their structure was shown by the molecular weight (ascertained by Raoult's method) and by the fact that both are converted almost quantitatively by hydrochloric acid into benzoic acid and hydroxylamine hydrochloride. It is, therefore, most probable that they form stereoisomerides of the formulæ

$$\begin{matrix} Ph{\cdot}C{\cdot}OEt \\ \| \\ HO{\cdot}N \end{matrix}, \qquad \begin{matrix} Ph{\cdot}C{\cdot}OEt \\ \| \\ N{\cdot}OH \end{matrix}.$$

To ascertain which of the compounds has the "syn" and which the "anti" configuration (compare Hantzsch, this vol., p. 312), both were treated with phosphorus pentachloride and subsequently with water at a low temperature (Abstr., 1891, 441). The α-compound was thus converted into ethyl phenylcarbamate, which could only be obtained from a compound having the "syn" configuration, by the following series of changes:—

$$\begin{matrix} Ph{\cdot}C{\cdot}OEt \\ \| \\ HO{\cdot}N \end{matrix}, \quad \begin{matrix} Ph{\cdot}C{\cdot}OEt \\ \| \\ Cl{\cdot}N \end{matrix}, \quad \begin{matrix} Cl{\cdot}C{\cdot}OEt \\ \| \\ Ph{\cdot}N \end{matrix}, \quad \begin{matrix} HO{\cdot}C{\cdot}OEt \\ \| \\ Ph{\cdot}N \end{matrix},$$

the last formula representing the tautomeric form of ethyl phenylcarbamate. The β-compound, on the other hand, yields a phosphate $PO(O{\cdot}N{:}CPh{\cdot}OEt)_3 + H_2O$, and not a substance of the configuration

$Ph\cdot\overset{\|}{C}(N\cdot Cl)\cdot OEt$, as would be expected from a compound having the "anti" configuration; in such a substance, however, the relative positions of Cl and OEt would be similar to that found in Sandmeyer's chlorimidoformates $R'\cdot\overset{\|}{C}(N\cdot Cl)\cdot OR''$, which show no tendency to intramolecular change. A further reason for the formation of a phosphate is found in the fact that, as already observed by Lossen, the β-compound behaves much more as an alcohol than an acid. Hence it appears that α-ethylbenzhydroximic acid is *ethylsynbenzhydroximic acid*, and the β-compound, *ethylantibenzhydroximic acid*.

The author next investigated the conditions under which stereoisomeric derivatives of benzhydroxamic acid are formed, and found that stereoisomerism occurs with compounds of the general formulæ $OR'\cdot CPh{:}N\cdot OH$ (an example of this being seen in the above ethylbenzhydroximic acids), $OR'\cdot CPh{:}N\cdot OR''$, but not with those having the general formula $OH\cdot CPh{:}N\cdot OR$. For this last fact the author accounts as follows: in the preparation of alkyl derivatives of the benzhydroxamic acids, and indeed of almost all oximes, there is formed in addition to the normal "oxygen ether" $OH\cdot CPh{:}N\cdot OR$, a certain quantity of the "nitrogen ether" $CPh\cdot O\cdot NR(OH)$, whence the benzhydroxamic acids must exist in the tautomeric forms

$$Ph\cdot\overset{\|}{C}(N)\cdot OH \quad , \qquad Ph\cdot C{:}O\cdot N(OH)\cdot N \quad .$$

The labile hydrogen atom, now in combination with the oxygen, now with the nitrogen, is the cause of the non-existence of both stereoisomerides of the benzhydroxamic acids, for if the derivative with the less favourable configuration were to be formed, it might at once yield the tautomeric form, which in passing back to the oxime form would naturally give the more favourable configuration. This series of reactions is represented by the following formulæ:—

$$Ph\cdot\overset{\|}{C}(N\cdot OH(R))\cdot OH \rightarrow Ph\cdot C{:}O\cdot N(H)\cdot HO(R) \leftarrow Ph\cdot\overset{\|}{C}(N\cdot HO\cdot(R))\cdot OH \quad .$$

In favour of this view is the fact that in the ethylation of the pure benzoyl derivative of benzhydroximic acid by the action of ethyl iodide on its silver salt, a certain quantity of the stereoisomeride is always obtained, showing that in some phase of the process the benzoyl derivative must have passed into the more favourable configuration.

The author has further investigated the compounds obtained by substituting chlorine for hydroxyl in the benzhydroxamic acids, that is, the derivatives of *benzenylchloroxime*, $CPhCl{:}N\cdot OH$, in order to ascertain whether these can exist in two stereoisomeric forms. The

results obtained with benzenylchloroxime paranitrobenzyl ether, $CPhCl{:}N{\cdot}OCH_2{\cdot}C_6H_4{\cdot}NO_2$, led to distinct conclusions, but benzenylchloroximeglycollic acid was found to exist in two well-marked stereoisomerides, probably corresponding with the configurations

$$\begin{matrix} Ph{\cdot}C{\cdot}Cl \\ \| \\ COOH{\cdot}CH_2{\cdot}O{\cdot}N \end{matrix} \quad , \qquad \begin{matrix} Ph{\cdot}C{\cdot}Cl \\ \| \\ N{\cdot}O{\cdot}CH_2{\cdot}COOH \end{matrix} \quad .$$

Of the detailed results given in the experimental portion of the paper, the following may be mentioned:—Ethylsynbenzhydroximic acid, when treated with hydrogen chloride in dry ethereal solution, yields the *hydrochloride*, which forms a white, crystalline meal melting at 90—91°; the *sodium* salt crystallises in nacreous plates, but a silver salt could not be prepared. The acid is, as already stated, converted by the action of phosphorus pentachloride and subsequent treatment with water into ethyl phenylcarbamate, melting at 49—50°; a small quantity of diphenylcarbamide is also obtained in the reaction. The *acetyl* derivative, $OEt{\cdot}CPh{:}N{\cdot}OAc$, is obtained by the action of acetic anhydride at the ordinary temperature, and forms large plates melting at 38—39°. The corresponding *paranitrobenzyl ether*, $OEt{\cdot}CPh{:}N{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, is prepared by the action of paranitrobenzyl chloride on the salts of ethylbenzhydroximic acid, and by treating the silver salt of the paranitrobenzyl ether of benzhydroximic acid with ethyl iodide; it crystallises in flat needles, and melts at 55—56°.

Ethylantibenzhydroximic acid yields a parallel series of derivatives: the *hydrochloride* melts at 95° with evolution of hydrogen chloride; the *acetyl* derivative crystallises in long needles melting at 57°; and the *paranitrobenzyl* derivative in yellow plates melting at 66—67°. The compound obtained by the action of phosphorus pentachloride, $PO(O{\cdot}N{:}CPh{\cdot}OEt)_3$, forms long prisms, and melts at 130—131°.

The following derivatives of benzhydroxamic acid have been prepared:—the *acetyl* derivative, $COPh{\cdot}NH{\cdot}OAc$ or $OH{\cdot}CPh{:}N{\cdot}OAc$, which crystallises in silky needles, and melts at 125°; the *benzoyl* derivative, $CPh{\cdot}O{\cdot}NH{\cdot}OBz$ or $OH{\cdot}CPh{:}N{\cdot}OBz$, already prepared by Lossen, and termed dibenzhydroxamic acid, which melts at 161°, and not as stated by the latter at 153°; the *paranitrobenzyl* derivative, crystallising in yellowish plates, and melting at 161°. In no case, as already mentioned in the theoretical portion of the paper, was any indication observed of the existence of stereometric isomerides of these compounds.

The investigation of the derivatives of benzenylchloroxime was commenced with the study of the action of phosphorus pentachloride on the benzoyl derivative of benzhydroxamic acid. The products obtained were, however, simply benzhydroxamic acid and benzoic chloride. The experiments were continued with the *paranitrobenzyl ether of benzenylchloroxime*, $CPhCl{:}N{\cdot}O{\cdot}CH_2{\cdot}C_5H_4{\cdot}NO_2$, which was prepared by the action of phosphorus pentachloride on the paranitrobenzyl ether of benzhydroxamic acid, and also from the *paranitrobenzyl ether of benzamidoxime* (which crystallises in sulphur-yellow plates, and melts at 105—106°), by diazotising in hydrochloric acid solution. The product crystallises in druses of white needles, and

melts at 92°; no formation of an isomeride was observed, although the mother liquors from the first preparation contain a very small quantity of a substance melting at 65°, the amount of which was insufficient for analysis. Better results were obtained with *benzenylchloroximeglycollic acid*, $CPhCl{:}N{\cdot}O{\cdot}CH_2{\cdot}COOH$, which is prepared by diazotising benzenylamidoxime in hydrochloric acid solution, and crystallises from alcohol in nacreous plates melting at 134—135°, readily soluble in alcohol, ether, and chloroform, sparingly in water, and insoluble in light petroleum. It dissolves in soda, the *sodium* salt soon separating out in silky crystals, which, on acidification, yield the original acid; if, however, these be allowed to remain in the acid solution, the crystals fall to a white powder. When the latter is treated with alcohol, a little of the original acid is extracted, but the residue is almost insoluble in all solvents, with the exception of acetic acid. It melts at 195°, has the same composition as the original acid, but stronger acid properties, and in all probability is the stereoisomeric benzenylchloroximeglycollic acid. Further experiments to test the truth of this view are in progress, and to determine, if this supposition prove correct, which possesses the "syn" and which the "anti" configuration. H. G. C.

Phenylthiocarbamide and Imidothiocarbamates. By A. Bertram (*Ber.*, **25**, 48—65).—The action of alkyl haloïds on disubstituted thiocarbamides has been frequently investigated (this Journ., 1875, 883; Abstr., 1879, 650; 1887, 43; 1888, 600, 944), but hitherto their action on mono-substituted carbamides has not been examined. The author therefore treated phenylthiocarbamide, obtained according to Clermont's method (*Ber.*, **9**, 446) with methyl iodide; the reaction takes place spontaneously when the two compounds are mixed, but it is preferable to add a little alcohol, and warm the mixture gently. On cooling, colourless crystals of the hydriodide of a new base separate; the base is isolated by the addition of sodium carbonate to the aqueous solution of the salt, extracting with ether, and allowing the ethereal solution to evaporate spontaneously. It is thus obtained in colourless, monosymmetric prisms ($a : b : c = 1{\cdot}3649 : 1 : 0{\cdot}8914$; $\beta = 64° 43'$), having the composition $C_8H_{10}N_2S$, and melting at 71°. On dry distillation, it yields chiefly aniline and methyl mercaptan, showing that the methyl group is united with the sulphur atom; on treatment with sulphuric acid, it yields methyl phenylthiocarbamate, $MeS{\cdot}CO{\cdot}NHPh$ (Will, Abstr., 1881, 905; 1882, 723), the elements NH being replaced by O. It therefore also contains the imido-group, and must be *methyl imidophenylthiocarbamate*, $SMe{\cdot}C(NH){\cdot}NHPh$. The *hydriodide* forms colourless needles melting at 147°, the *nitrate* a white, crystalline powder melting at 113°, the *picrate* deep-yellow, rectangular plates melting at 175°, the *platinochloride*, $(C_8H_{10}N_2S)_2,H_2PtCl_6$, an orange, crystalline precipitate. It yields two *sulphates*: $C_8H_{10}N_2S,H_2SO_4$ and $(C_8H_{10}N_2S)_2,H_2SO_4$, both of which melt at 171°, the former giving a brown, the latter a colourless liquid.

Methyl imidophenylthiocarbamate readily reacts with another molecule of methyl iodide, forming the hydriodide of *methyl imidomethyl-*

phenylthiocarbamate, SMe·C(NH)·CMePh, which is a pale-yellow oil, and does not crystallise at 0°. Its *hydriodide* melts at 184°; the *picrate* forms yellow prisms, which have a paler colour than the picrate of the preceding base, as is also the case with the *platino*-chloride, $(C_9H_{12}N_2S),H_2PtCl_6$. On treatment with sulphuric acid, the base is converted into *methyl methylphenylthiocarbamate*, SMe·CO·NMePh, which crystallises from dilute alcohol in slender plates melting at 54°; the formation of this compound shows that the second methyl radicle has entered the amido-, and not the imido-group. The latter group may, however, also be methylated by heating the base with anhydrous methyl iodide, the hydriodide thus formed being treated with sodium carbonate. *Methyl methylimido-methylphenylthiocarbamate*, SMe·C(NMe)·NMePh, may be distilled with but slight decomposition under the ordinary pressure, when it boils at 265°; its *hydriodide* melts at 184°, and is much more soluble than those of the foregoing bases; the *picrate* has a lemon-yellow colour, and melts at 126°, whilst the *platinochloride* melts at 174° with decomposition. When the base is heated with sulphuric acid, it yields the same product as the dimethylated compound, namely methyl methylphenylthiocarbamate, SMe·CO·NMePh, the group NMe being replaced by O.

The corresponding ethyl derivatives may be obtained in an exactly similar manner from phenylthiocarbamide and ethyl iodide. *Ethyl imidophenylthiocarbamate*, SEt·C(NH)·NHPh, is a colourless, odourless liquid, which readily gives off ethyl mercaptan; its hydriodide melts at 103°, and its picrate at 196°. With ethyl iodide, it yields the *hydriodide of ethyl imidoethylphenylthiocarbamate*,

SEt·C(NH)·NEtPh,HI,

which may be obtained in crystals from benzene; the *picrate* melts at 170°, and the *platinochloride* at 148° with decomposition. *Ethyl ethyl-imidoethylphenylthiocarbamate*, SEt·C(NEt)·NEtPh, is a yellowish, colourless oil, and boils at 273°; its *picrate* melts at 96°, and its *platinochloride* at 135°, decomposition commencing at a higher temperature.

The action of ethyl iodide on triethylthiocarbamide has been examined by Grodski, who believed at first that the product was tetrethylthiocarbamide, but afterwards stated that it was an imido-thiocarbamate (Abstr., 1882, 823). The author finds that methyl iodide reacts readily with methyl symmetrical diphenylthiocarbamide, forming the hydriodide of a base which has the composition $C_{15}H_{16}N_2S$. It is a yellowish oil, boiling above 300°, almost without decomposition, and on treatment with carbon bisulphide is converted into *methyl methylphenyldithiocarbamate*, SMe·CS·NMePh, which is also formed by the action of carbon bisulphide on methyl methyl-imidomethylphenylthiocarbamate, and crystallises in slender, colourless plates, melting at 88°. The base $C_{15}H_{16}N_2S$ must therefore be *methyl phenylimidomethylphenylthiocarbamate*, SMe·C(NPh)·NMePh.

Ethylene bromide acts on diphenylthiocarbamide with formation of a hydrothiohydantoïn (Will, Abstr., 1881, 906) and on thiocarbamide itself, with formation of the compound $C_2H_4[S·C(NH)·NH_2]_2$

(Andreasch, Abstr., 1883, 665). The monosubstituted thiocarbamides act in a manner similar to the unsubstituted compounds; thus phenylthiocarbamide forms a crystalline substance having the constitution $C_2H_4[S{\cdot}C(NH){\cdot}NHPh]_2$ or $C_2H_4[S{\cdot}C(NPh){\cdot}NH_2]_2$, which melts at 139°, is insoluble in water, but soluble in alcohol, ether, and benzene. Its *hydrochloride* and *hydrobromide* form slender needles, and melt at 218° and 214° respectively; the *platinochloride*, $C_{16}H_{18}N_4S_2,H_2PtCl_6$, has a pale reddish-brown colour, and melts at 150° with decomposition; the *picrate*, $C_{16}H_{18}N_4S_2 + 2C_6H_3N_3O_7$, is a crystalline precipitate, and melts at 196°.

Bromine-water acts on a solution of methyl imidophenylthiocarbamate in hydrobromic acid, yielding a mixture of symmetrical tribromaniline, dibromo- and tribromo-phenylcarbamide, which separates out as an insoluble precipitate, whilst the solution contains methylsulphonic acid, obtained by the oxidation of the mercaptan group. *Dibromophenylcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3Br_2$ [NH : Br : Br = 1 : 2 : 4], and *tribromophenylcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_2Br_3$ [NH : Br : Br : Br = 1 : 2 : 4 : 6], may also be obtained directly from phenylcarbamide, and melt at 201° and 270° respectively; both distil at a high temperature almost unchanged.

When methyl mercaptan, obtained by the decomposition of some of the above compounds, was led into alcohol containing freshly precipitated mercuric oxide, a mixture of mercuric methylmercaptide with mercuric oxide was obtained. To estimate the amount of methylmercaptan, this must be dissolved in acetic acid, which yields a double salt of mercuric methylmercaptide and acetate,

$$Hg(MeS)_2,2Hg(OAc)_2;$$

on the addition of mercuric chloride, the compound MeSHgCl is precipitated, and may be separated and weighed. H. G. C.

Methylenedibenzamide and Analogous Compounds. By H. Thiesing (*J. pr. Chem.* [2], **44**, 570—571).—Methylenedibenzamide was prepared by adding concentrated sulphuric acid to a hot solution of solid paraformaldehyde (1 mol. proportion) and benzonitrile (2 mol. proportions) in glacial acetic acid, cooling, mixing with water, and recrystallising from hot alcohol; it melts at 218° (uncorr.).

Methylenedinitrodibenzamide is obtained when nitrobenzonitrile is used in the above prescription; it crystallises in slender needles, and melts at 214° (uncorr.). *Methylenediparatoluylamide*, obtained when paratolunitrile is used, crystallises in bundles of slender needles, melts at 217° (uncorr.), and dissolves in alcohol, ether, chloroform, and strong acids; it is decomposed by hot hydrochloric acid with formation of paratoluic acid. *Methylenediorthotoluylamide* is a gelatinous mass which melts at 199° (uncorr.). *Methylenedi-α-toluylamide* is obtained when benzyl cyanide is used; it crystallises from hot alcohol in slender, prismatic needles, and melts at 211° (uncorr.).

A. G. B.

Derivatives of Phenylamidoacetic Acid. By A. Kossel (*Ber.*, **24**, 4145—4156).—*Methyl phenylamidoacetate hydrochloride*,

$$NH_3Cl{\cdot}CHPh{\cdot}COOMe,$$

is prepared by dissolving phenylamidoacetic acid in methyl alcohol, and saturating the solution with hydrogen chloride; it is purified by crystallisation from water, melts at 224°, and dissolves in alcohol or benzene, but is insoluble in ether. The *ethyl salt*, $NH_3Cl{\cdot}CHPh{\cdot}COOEt$, is prepared in a similar manner to the preceding compound, and crystallises in long, colourless needles melting at 197°. The *allyl salt*, $NH_3Cl{\cdot}CHPh{\cdot}COO{\cdot}C_3H_5$, crystallises from alcohol, on the addition of ether; it darkens at 220°, and melts at 226° with decomposition. The *amyl* derivative, $NH_3Cl{\cdot}CHPh{\cdot}COO{\cdot}C_5H_{11}$, crystallises in colourless needles which melt at 154°. The free ethereal salts are obtained from the hydrochlorides by dissolving these in water, covering the solution with a layer of ether, and cautiously adding potash, the solution being continually shaken; or the hydrochlorides may be suspended in ether, and decomposed by means of argentic oxide. The ethereal solution is then dried over barium oxide, the ether removed by distillation, and the residue purified by fractionation in a vacuum.

Methyl phenylamidoacetate, $NH_2{\cdot}CHPh{\cdot}COOMe$, crystallises from light petroleum in long, slender needles which melt at 32°. The *ethyl salt*, $NH_2{\cdot}CHPh{\cdot}COOEt$, is a pale yellow, oily liquid boiling at 257°. The *allyl* and *amyl* salts are colourless, viscid liquids, which are not decomposed by boiling with water.

Phenylamidoacetic anhydride, $CHPh<^{CO\cdot NH}_{NH\cdot CO}>CHPh$, is obtained by heating methyl phenylamidoacetate at 160°, and is a colourless crystalline powder, insoluble in ordinary media; it darkens at 250°, and melts at 274° with decomposition. The molecular weight of this compound could not be determined, as it undergoes decomposition at high temperatures.

Ethyl phenyluramidoacetate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}COOEt$, is prepared by the action of potassium cyanide in aqueous solution on ethyl phenylamidoacetate hydrochloride; it melts at 139°, and yields α-phenylhydantoïn, $CHPh<^{NH\cdot CO}_{CO\cdot NH}$, on hydrolysis in aqueous or alkaline solution.

With benzoic chloride and potash, ethyl phenylamidoacetate hydrochloride yields *ethyl phenylhippurate*, $NHBz{\cdot}CHPh{\cdot}COOEt$, which is soluble in alcohol or ether, and melts at 84°. The free *acid* melts at 174°. The *silver salt* crystallises in white needles.

Ethyl phenylthiouranilidacetate, $NHPh{\cdot}CS{\cdot}NH{\cdot}CHPh{\cdot}COOEt$, prepared from ethyl phenylamidoacetate and phenylthiocarbimide, melts at 162°; on hydrolysis in acid or alkaline solution, it yields *diphenylthiohydantoïn*, $CHPh<^{NH\cdot CS}_{CO\cdot NPh}$, which melts at 233°.

Ethyl phenyluranilidacetate, $NHPh{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}COOEt$, is obtained as a colourless, crystalline powder by treating ethyl phenylamidoacetate with phenylcarbimide in ethereal solution; it melts at 165°, and on hydrolysis with dilute potash, yields the acid $NHPh{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}COOH$, which melts at 154°, and is also formed by heating diphenylthiohydantoïn with potash.

Ethyl ethylurethanophenylacetate, $COOEt{\cdot}NH{\cdot}CHPh{\cdot}COOEt$, is prepared by the mutual action of ethyl phenylamidoacetate (2 mols.) and ethyl chloroformate (1 mol.) in ethereal solution; it crystallises from dilute alcohol in long, white needles which melt at 54°. *Ethylurethanophenylacetic acid*, $COOEt{\cdot}NH{\cdot}CHPh{\cdot}COOH$, is formed by the hydrolysis of the preceding compound with dilute potash, and melts at 155°.

By the action of nitrous acid on methyl phenylamidoacetate hydrochloride, methyl phenylhydroxyacetate is produced, whilst the corresponding ethyl salt is formed with nitrous acid and ethyl phenylamidoacetate.

Ethyl phenylamidoacetate nitrite, $NO_2{\cdot}NH_3{\cdot}CHPh{\cdot}COOEt$, is formed from ethyl phenylamidoacetate hydrochloride and argentic nitrite in ethereal solution; it crystallises in small, white needles, which melt at 59° with evolution of nitrogen. Attempts to obtain ethyl phenyldiazoacetate from the preceding compound were unsuccessful.

J. B. T.

The Stereoisomeric and Polymeric Cinnamic Acids. By C. Liebermann (*Ber.*, **25**, 90—95).—F. Stohmann has furnished the author with the heats of combustion of allocinnamic acid, α- and β-truxillic acid, and polycinnamic acid, and compared them with the heat of combustion of cinnamic acid. Of these compounds, the most labile, namely, allocinnamic acid, gives the highest heat of combustion; cinnamic acid gives 5·2 cal. less. A similar difference is observed in the case of the labile and stable forms of other substances.

The polycinnamic acids give lower heats of combustion than cinnamic acid; the lowest number being obtained in the case of the most stable acid, also the one of highest molecular weight. The relations of the heats of combustion calculated for the formula $C_9H_8O_2$ are as follows:—

Allocinnamic acid ..	1047·6 cal.	β-Truxillic acid..	1040·1 cal.
Cinnamic acid	1042·3 „	α-Truxillic acid..	1035·3 „
	Polycinnamic acid.....	1021·0 cal.	

From the comparison of the heats of formation of cinnamic acid and allocinnamic acid taken in conjunction with the values obtained for other stereoisomeric unsaturated acids, it appears, at first sight, easy to determine which of the two configurations,

$$\text{I.}\ \begin{matrix} Ph{\cdot}C{\cdot}H \\ \| \\ H{\cdot}C{\cdot}COOH \end{matrix} \quad \text{and} \quad \text{II.}\ \begin{matrix} Ph{\cdot}C{\cdot}H \\ \| \\ COOH{\cdot}C{\cdot}H \end{matrix},$$

represents cinnamic, and which allocinnamic, acid. The author, after a searching inquiry into the matter, comes to the conclusion that neither the physical nor chemical properties of cinnamic acid provide means of determining its formula with certainty.

If the cinnamic acids be compared with stereoisomerides of the fatty acid series, then the physical and chemical properties seem to indicate that allocinnamic acid : cinnamic acid as erucic acid : brassidic acid, angelic acid : tiglic acid, and isocrotonic acid : crotonic acid. Then, according to Wislicenus' well-founded supposition, the experiments of Holt (*Ber.*, **24**, 4120) on erucic and brassidic acid

derivatives show that the fatty acids must be represented by the axial symmetrical formula I, the elaïdin acids by the plane symmetrical formula II—

$$\text{I.}\ \begin{matrix} X\cdot C\cdot H \\ \| \\ H\cdot C\cdot COOH \end{matrix}, \qquad \text{II.}\ \begin{matrix} X\cdot C\cdot H \\ \| \\ COOH\cdot C\cdot H \end{matrix},$$

from which we may conclude that allocinnamic acid is represented by formula I, and cinnamic acid by formula II.

If, however, the fundamental principle of Wislicenus' theory be considered, namely, that the revolution of the carbon atom system, to which the stereoisomerism is referred, is a consequence of the opposite chemical affinities of the radicles combined with it, so that a positive radicle of one carbon atom approaches a negative radicle of the other, and *vice versâ*, then the cinnamic acids differ from the fatty acids. For if, in the latter, the alkyl is considered positive, the phenyl in the former must be considered negative. From this point of view, the cinnamic acids must be compared with those unsaturated acids in which the two doubly-linked carbon atoms are each combined with a hydrogen atom and a negative group; then the analogues of the cinnamic acids are fumaric and maleïc acid. Now, from its physical and chemical properties, allocinnamic acid corresponds with maleïc acid, and cinnamic acid with fumaric acid, whence the former should be represented by formula II, the latter by formula I—the direct opposite to the conclusion previously arrived at.

The author concludes that other methods must be employed to settle the question. The determination of which two of the four monobromocinnamic acids, $C_2HPhBr\cdot COOH$, are derived from cinnamic acid, and the investigation of the dihalogen derivatives prepared from phenylpropiolic acid, are likely to throw some light on the matter. But the experiments are difficult, since the reduction (resubstitution) does not take place under all conditions; thus, in alkaline solution, the cinnamic derivatives yield hydrocinnamic acid, and in acid solution, allocinnamic acid easily undergoes isomeric change to cinnamic acid. E. C. R.

Diiodocinnamic Acid. By C. Liebermann and H. Sachse (*Ber.*, **24**, 4112—4118; compare Abstr., 1891, 1483).—Diiodocinnamic acid, $CPhI{:}CI\cdot COOH$, is readily prepared by mixing phenylpropiolic acid with 10 per cent. of anhydrous ferrous iodide, and adding iodine in carbon bisulphide solution; the reaction requires 10 days for completion; the acid crystallises in the monosymmetric system, $a : b : c = 0{\cdot}2093 : 1 : 0{\cdot}5008$; $\beta = 69°\ 38{\cdot}5'$. The sodium salt crystallises with $3H_2O$; the *calcium salt* is deposited from water in lustrous plates. On heating the silver salt at about 70°, phenyliodoacetylene, $CPh{:}CI$ is formed, the silver combining with a β-iodine atom. *Triiodocinnamene*, $CPhI{:}CI_2$ is formed by the addition of iodine to the preceding compound, and crystallises from alcohol, on the addition of water, in colourless needles melting at 108°. The same compound is also obtained by the action of iodine, in potassium iodide solution, on the silver salt of phenylacetylene.

Diiodostearolic acid, $C_{18}H_{32}O_2I_2$, is prepared in a similar manner to

diiodocinnamic acid, but the reaction proceeds more slowly, and the compound is difficult to purify; it crystallises from alcohol on the addition of water, and melts at 50—51°. The *ammonium salt* crystallises in small, lustrous plates; the *silver salt* decomposes at 100°, and yields an iodo-acid, which is being further investigated.

Diiodobehenolic acid, $C_{22}H_{40}O_2I_2$, is prepared like the preceding compound, and melts at 47°; in appearance, it closely resembles behenolic acid. The *silver salt* decomposes on heating with the formation of silver iodide.

The authors have shown with what difficulty unsaturated acids form iodine additive compounds; they point out the bearing of this fact on the interpretation of the "iodine values" obtained in the analysis of oils and fats by Hübl's method; they have treated a number of pure unsaturated acids with Hübl's reagent, but in no case succeeded in isolating any iodine additive compound; the reaction appears to be very complicated, and may consist in the addition of chlorine to the unsaturated acid. J. B. T.

An Isomeric Dichlorhydrin Metahydroxybenzoate. By C. Göttig (*Ber.*, **24**, 3845—3848; see also Abstr., 1891, 1482).—The author has examined the amorphous fatty compound obtained, together with β-dichlorhydrin metahydroxybenzoate, by the action of hydrogen chloride on a solution of metahydroxybenzoic acid in glycerol. He believes this compound to be a stereoisomeride of β-dichlorhydrin metahydroxybenzoate, and names it iso-β-dichlorhydrin metahydroxybenzoate.

Iso-β-dichlorhydrin metahydroxybenzoate is obtained when the above reaction is allowed to proceed at a temperature of 120—140°. It is purified by crystallisation from absolute alcohol, melts at 76—79°, is easily soluble in alcohol, ether, benzene, and carbon bisulphide, sparingly so in cold water, and forms nodular aggregates or needles. When boiled with water, it is converted into its crystalline isomeride. When warmed with alkalis, it is decomposed into epichlorhydrin and metahydroxybenzoic acid, the latter undergoing partial decomposition. E. C. R.

Phenyl-α-hydroxycrotonic Acid. By F. Tiemann (*Ber.*, **24**, 4065—4073).—In this paper, an account is given of the work already done by others on phenyl-α-hydroxycrotonic acid (Matsmoto, this Journal, 1876, i, 80; Peine, Abstr., 1884, 1344; Pinner and Lifschütz, *ibid.*, 1887, 1054), and the outline of an investigation carried out at the author's suggestion by Biedermann (see following abstract). A. R. L.

Derivatives of Phenyl-α-hydroxycrotonic Acid. By J. Biedermann (*Ber.*, **24**, 4074—4082; compare preceding abstract).—*γ-Phenyl-γ-bromo-α-hydroxybutyric acid*,

$$CHPhBr{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH,$$

separates as a crystalline mass when phenyl-α-crotonic acid is dissolved in aqueous hydrogen bromide saturated at 0°; when crystallised from alcohol, it forms white needles, melts at 126°, and is readily soluble in

alcohol, ether, and chloroform, but insoluble in light petroleum. *γ-Phenyl-α-hydroxybutyro-γ-lactone*, $CHPh<\begin{matrix}CH_2\cdot CH\cdot OH\\ |\\ O-CO\end{matrix}$, is obtained:—(1) When the bromo-acid is boiled with water, the solution neutralised with sodium carbonate, and extracted with ether; (2) when the bromo-acid is heated with dilute sodium carbonate solution; (3) when the same compound is treated with sodium amalgam, and the solution acidified from time to time with sulphuric acid; (4) when phenyl-α-hydroxycrotonic acid is boiled with dilute sodium carbonate. It crystallises in broad needles, melts at 39°, and dissolves readily in most solvents, but is only sparingly soluble in water and light petroleum; its solutions have a neutral reaction. *γ-Phenyl-αγ-dihydroxybutyric acid* cannot be prepared, as it readily passes into the lactone, but its salts are obtained when the lactone is dissolved in solutions of the alkalis or alkaline earths. The *hydrazide*,

$$OH\cdot CHPh\cdot CH_2\cdot CH(OH)\cdot CO\cdot N_2H_2Ph,$$

is obtained by boiling an alcoholic solution of the lactone and phenylhydrazine (equal mols.) for 6—8 hours. It crystallises from benzene containing a little alcohol in white needles, melts at 133°, is decomposed by alkalis, and gives a reddish-violet colour with ferric chloride.

γ-Phenyl-α-acetoxycrotonic acid, $CHPh{:}CH\cdot CH(OAc)\cdot COOH$, is prepared by heating well dried phenyl-α-hydroxycrotonic acid with acetic chloride in molecular proportion until the evolution of hydrogen chloride ceases; the product, after cooling, is collected, and when repeatedly crystallised from glacial acetic acid forms bright, yellow needles, melts at 118°, and is readily soluble in alcohol and ether, but insoluble in cold water, benzene, light petroleum, and chloroform. Boiling alkalis hydrolyse it.

γ-Phenylcroton-α-lactone, $CHPh{:}CH\cdot CH<\begin{matrix}O\\ |\\ CO\end{matrix}$, is produced when dry phenyl-α-hydroxycrotonic acid is boiled with somewhat more than one molecular proportion of acetic anhydride in a reflux apparatus for five hours; it crystallises from glacial acetic acid in bright red leaflets, melts at 93°, and is sparingly soluble in boiling water, readily so in alcohol and ether. On adding ferric chloride to its hot aqueous solution, a red precipitate is produced, which redissolves to a green solution on the addition of sodium carbonate; it is reconverted into the acid by alkalis. The *phenylhydrazide*,

$$CHPh{:}CH\cdot CH(OH)\cdot CO\cdot N_2H_2Ph,$$

obtained by heating an alcoholic solution of the α-lactone and phenylhydrazine (equal mols.) on the water-bath for two hours, crystallises from alcohol in white needles, melts at 154°, and is insoluble in water, benzene, and light petroleum. It dissolves in alkalis undergoing hydrolysis, but in concentrated sulphuric acid without decomposition. The *anilide*, $CHPh{:}CH\cdot CH(OH)\cdot CO\cdot NHPh$, formed by heating an alcoholic solution of the α-lactone and aniline on the water-bath for an hour, crystallises from alcohol in lustrous needles, and melts at 150°. The *amide*, $CHPh{:}CH\cdot CH(OH)\cdot CONH_2$, prepared by adding an excess

of alcoholic ammonia to the finely-powdered α-lactone, allowing the mixture to remain for several days, and finally digesting it on the water-bath for 4—5 hours, crystallises from boiling water in white needles, melts at 125° to a blue liquid, is soluble in alcohol, but only sparingly so in benzene, and is hydrolysed by alkalis and ammonia.

When an alcoholic solution of phenyl-α-hydroxycrotonic acid and phenylhydrazine (equal mols.) is boiled in a reflux apparatus for six hours, a compound $C_{16}H_{14}N_2O$, melting at 98°, is formed, which yields a bromo-derivative $C_{16}H_{13}BrN_2O$, melting at 145°, and is, perhaps, a derivative of phenylpyridazone (Ach, Abstr., 1890, 70) of the formula $CHPh<^{CH=CH}_{NH\cdot NPh}>CO$.

A. R. L.

A New Method of Preparing the Amide, Anilide, and Phenylhyrazide of Mandelic Acid. By J. Biedermann (*Ber.*, **24**, 4083—4084).—When finely powdered mandelic acid (dried at 100°) is heated with an excess of acetic anhydride for six hours in a reflux apparatus, the product poured into water, and the resulting solution, after neutralising with sodium carbonate, extracted with ether, the corresponding α-lactone remains after distilling the ether from the extract, as a syrup which solidifies to an amorphous mass on being left over sulphuric acid. Mandelamide, agreeing with Tiemann and Friedländer's description (Abstr., 1882, 56), is obtained when the α-lactone is digested with an excess of ammonia in a closed flask at 100° for six hours; mandelanilide (Reissert and Kayser Abstr., 1891, 438), when the same compound is similarly digested with an alcoholic solution of aniline for 10 hours; and mandelic phenylhydrazide melting at 182° (Reissert and Kayser, Abstr., 1890, 155), when it is heated in a reflux apparatus with an alcoholic solution of phenylhydrazine in molecular proportion for five hours.

A. R. L.

Paraxylalphthalide. By A. Ruhemann (*Ber.*, **24**, 3964—3976).—Paratolylacetic acid, like phenylacetic and metatolylacetic acids (Abstr., 1891, 200), readily unites with phthalic anhydride on heating, with elimination of water and carbonic anhydride and formation of a phthalide. The two compounds are heated together with a little anhydrous sodium acetate, first at 230°, and after a time at 255°, the cooled product being powdered and recrystallised from boiling alcohol. *Paraxylalphthalide*, $CO<^{C_6H_4}_{O\ \ \ \ -}>C:CH\cdot C_6H_4Me$, is thus obtained in beautiful, yellow needles melting at 151°, sparingly soluble in alcohol and ether, more readily in boiling benzene, and easily in hot acetic acid. It combines directly with bromine, forming a *dibromide*, $C_{16}H_{12}Br_2O_2$, which crystallises from ether or chloroform in white, lustrous prisms, and melts at 150° with violent evolution of bromine and hydrogen bromide.

When fused with potash, paraxylalphthalide yields the potassium salt of *paramethyldeoxybenzoïnorthocarboxylic acid*,

$$C_6H_4Me\cdot CH_2\cdot CO\cdot C_6H_4\cdot COOH;$$

the free acid crystallises from alcohol in white, lustrous plates, and melts at 126°. By the action of hydroxylamine, it probably first yields the oxime, the latter then losing water, forming an *oximidolactone*, $C_6H_4 \cdot \underset{CO\cdot O\cdot N}{\overset{|}{\underset{||}{C}}}\cdot CH_2\cdot C_7H_7$, which crystallises in slightly pink needles and melts at 126°. Alcoholic ammonia at 100° converts paraxylalphthalide into the *amide* of the above acid, $C_6H_4Me\cdot CH_2\cdot CO\cdot C_6H_4\cdot CONH_2$, which melts at 135—140°, and very readily loses water, forming *paraxylalphthalimidine*, $CO<\begin{matrix}C_6H_4\\NH-\end{matrix}>C{:}CH\cdot C_7H_7$; this substance crystallises in well developed, yellow, rhombic prisms, and melts at 203—204°. When subjected to the action of phosphorus and hydriodic acid, it takes up 2 atoms of hydrogen forming *paraxylylphthalimidine*,

$$CO<\begin{matrix}C_6H_4\\NH-\end{matrix}>CH\cdot CH_2\cdot C_7H_7,$$

which crystallises from hot water in long, lustrous needles and melts at 149°. Towards dehydrating agents it behaves in a manner similar to benzylphthalimidine (Abstr., 1888, 143), yielding a compound of unknown constitution. Paraxylalphthalimidine is acted on by nitrous acid in chloroform solution, with formation of *nitroparaxylalphthalimidine*, $CO<\begin{matrix}NH-\\C_6H_4\end{matrix}>C{:}C(NO_2)C_7H_7$, an intermediate dinitro-additive compound being probably formed. The nitro-compound forms lustrous, yellow needles, and melts at 227° with decomposition. Nitrous acid also gives with paraxylalphthalide, in the first place, an unstable *dinitro*-additive compound, $\begin{matrix}CO\cdot O\\|\\C_6H_4\end{matrix}>C(NO_2)\cdot CH(NO_2)\cdot C_7H_7$, which melts with vigorous decomposition at 240°, and on boiling with alcohol, yields *nitroparaxylalphthalide*, $\begin{matrix}CO\cdot O\\|\\C_6H_4\end{matrix}>C{:}C(NO_2)\cdot C_7H_7$. The latter melts at 205—207°, decomposing at the same time, like the nitro-derivatives of metaxylalphthalide and benzalphthalide, into phthalic anhydride and paratolyl isocyanate. With boiling aqueous potash, it yields phthalic anhydride, and a substance which is apparently paratolylnitromethane.

By the action of phosphorus and boiling hydriodic acid, nitroparaxylalphthalide is, like the corresponding metaxylal- and benzal-derivatives, converted into an isomeride of paraxylalphthalide, namely, *isoparaxylalphthalide*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_7H_7\\|\\CO\cdot O\end{matrix}$; the latter forms white, prismatic crystals, melts at 116°, and is converted by alcoholic ammonia at 100° into *isoparaxylalphthalimidine*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_7H_7\\|\\CO\cdot NH\end{matrix}$, which crystallises in long, pointed prisms, and melts at 226—228°. When this substance is treated with phosphorus oxychloride at 100°, it yields *α-chloro-β-paratolylisoquinoline*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_7H_7\\|\\Cl{:}N\end{matrix}$, which

crystallises in lustrous plates, melts at 70—71°, and on reduction with phosphorus and hydriodic acid, yields *β-paratolylisoquinoline*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_7H_7\\ CH\cdot N\end{matrix}$. The latter crystallises from light petroleum in lustrous, white needles, melts at 78°, and has basic properties. The *hydrochloride* and *hydrobromide* form compact, white prisms, the *hydriodide* long needles, the *chromate* reddish needles, the *picrate* yellow needles, and the *platinochloride*, $(C_{16}H_{13}N)_2,H_2PtCl_6$, yellowish-brown, arborescent groups of needles. H. G. C.

Preparation of Nitrososulphonic Acids. By H. Limpricht (*Ber.*, **25**, 75—77).—The method consists in adding metanitrobenzenesulphonic chloride in small quantities at a time to a concentrated solution of sodium sulphite. The sulphonic chloride dissolves with slight development of heat, and the action is completed by heating on the water-bath. Care must be taken that the mixture does not become acid, and from time to time a few drops of concentrated sodium hydroxide is added. The solution is evaporated to dryness, extracted with alcohol (95 per cent.), the alcohol distilled off, the dry residue extracted with absolute alcohol, and the alcoholic solution evaporated to dryness. The product is treated in this way until it contains neither sulphate nor chloride; or the pure substance may be obtained by dissolving the product obtained by extraction with alcohol in water, adding silver nitrate until all the chloride is precipitated, and then converting the nitrososulphonic acid into silver salt by the further addition of silver nitrate.

Sodium nitrosobenzenesulphonate, $NO\cdot C_6H_4\cdot SO_3Na + 2H_2O$, is easily soluble in water and hot alcohol, crystallises in crusts of small, lustrous leaflets, gives Liebermann's reaction, and when treated with potassium permanganate in aqueous solution, is converted into nitrobenzenesulphonic acid. The *silver* salt, which is precipitated in slender, yellowish needles on adding silver nitrate to a dilute solution of the sodium salt, is somewhat sparingly soluble in boiling water, and crystallises, on cooling, in long, slender needles. The *barium* salt crystallises in long, white needles, is easily soluble in cold water, and explodes when heated on platinum foil. The *free acid*, obtained by decomposing the silver salt with hydrochloric acid, crystallises from concentrated solutions in white needles, and is converted into a resin, insoluble in water, by evaporating its solution with hydrochloric or sulphuric acids.

The nitroso-acids obtained from orthonitrotoluenesulphonic acid and nitronaphthalenesulphonic acid by this method have properties similar to the above.

Experiments to obtain the nitroso-acids from the salts of the nitrosulphonic acids, instead of from the chlorides, gave negative results; as also did experiments to obtain the nitroso-acids from the chlorides of ortho- and meta-nitrobenzoic acids. E. C. R.

Action of Sulphurous Acid on Isonitroso-compounds. By M. Schmidt (*J. pr. Chem.* [2], **44**, 513—535; compare Abstr., 1887,

549, 635; 1888, 913; 1890, 1305).—*Benzylamidosulphonic acid*, $C_7H_7{\cdot}NH{\cdot}SO_3H + \frac{1}{2}H_2O$, is the product of the action of sulphurous anhydride on an aqueous solution of β-benzylhydroxylamine hydrochloride (Behrend and Leuchs, *Annalen*, **257**, 223; Abstr., 1889, 500, 703); it forms white, crystalline aggregates, melts at 180° with decomposition, and is unstable, the sulphonic group readily forming sulphuric acid with the water of crystallisation; its alkali salts are soluble in water.

Dibenzylamidosulphonic acid, $N(C_7H_7)_2{\cdot}SO_3H + H_2O$, is prepared by adding finely-powdered β-dibenzylhydroxylamine (Behrend and Leuchs, *loc. cit.*) to a boiling 40 per cent. aqueous solution of sodium hydrogen sulphite, as long as it dissolves pretty freely, and filtering while hot. A copious separation of felted, thin, tabular crystals, together with some needles, occurs on cooling the solution; the tables are separated from the needles by cold water, which dissolves the former, the solution yielding the sulphonic acid on the addition of hydrochloric acid. When freshly prepared, it is soluble in cold water, but, after drying, it is only soluble in hot water, whereby it loses sulphur; the solution is precipitated by hydrochloric acid, but not by acetic acid. It melts at 160°, or, when quickly heated, at 170° with decomposition. It dissolves in ammonia, hot alcohol, and glacial acetic acid; the ammoniacal solution does not reduce silver nitrate. Attempts to prepare its salts were unsuccessful on account of its instability; when alcoholic silver nitrate is added to its solution in alcohol, silver sulphate is precipitated; ammonia and sodium hydroxide both give white precipitates, soluble in excess, when added to its solution. When the ammonia precipitate is dissolved in nitric acid, white needles of *dibenzylamine nitrate*, melting at 190° and soluble in water, crystallise out.

When an aqueous solution of acetoxime is saturated with sulphurous anhydride, amidosulphonic acid (m. p. 200°) is formed (compare Pechmann, Abstr., 1887, 1103; 1888, 146).

No definite results were obtained from the action of sulphurous anhydride on nitrosophenol, nitrosoresorcinol, or dinitroso-orcinol; a brown liquid, which strongly reduced ammoniacal silver nitrate, was produced in each case, but attempts to crystallise the contained compound failed. Nitrosothymol is not attacked by sulphurous acid, whether applied in the form of sulphurous anhydride in water, or of sodium hydrogen sulphite.

α-Amido-β-naphtholsulphonic acid is best obtained by adding finely-powdered α-nitroso-β-naphthol to a boiling 35 per cent. solution of sodium hydrogen sulphite, as long as it dissolves to a bright, yellow solution, filtering, and adding concentrated hydrochloric acid to the hot filtrate; prismatic needles separate when the liquid cools, and are purified by recrystallising from sodium hydrogen sulphite solution, when they are obtained as pale yellow needles, which become reddish when exposed to air. The acid is insoluble in water, alcohol, ether, and benzene, but dissolves in sodium acetate solution, ammonia, and other alkalis, from which it is precipitated by hydrochloric acid; it also dissolves in concentrated sulphuric acid. Its alkaline solutions readily oxidise on exposure to air, and it reduces am-

moniacal silver solutions very readily. When it is heated with concentrated hydrochloric acid at 150—160° in a sealed tube, the sulphur is entirely converted into sulphuric acid, ammonia and a black nitrogenous mass being at the same time produced. When heated on platinum foil, it intumesces and decomposes with evolution of a deep violet vapour. The author compares the above properties with those of the four known amido-β-naphtholsulphonic acids, and shows that his acid is different from any of the others.

When oxidised, α-amido-β-naphtholsulphonic acid yields sulphuric acid, but no other definite product has been isolated. No success attended efforts to prepare its salts. When treated with sodium nitrite and sulphuric acid, it yields yellow needles of what seems to be a nitro-derivative.

α-Amido-β-naphtholsulphonic acid is also the main product when sulphurous acid acts on chloro-β-naphthaquinone-α-oxime and on trichloro-β-ketohydronaphthalene-α-oxime (Zincke, Abstr., 1890, 1146).

β-Amido-α-naphtholsulphonic acid is obtained by adding hydrochloric acid to a solution of β-nitroso-α-naphthol in 35 per cent. sodium hydrogen sulphite; it crystallises from dilute sodium hydrogen sulphite solution in white aggregates of needles (with $1\frac{1}{2}$ mols. H_3O), which become pale-grey in air. It is more stable than the isomeride described above; it can be heated at 120° without decomposition, is difficultly combustible, and does not lose sulphuric acid when treated with oxidising agents. The whole of its sulphur is not removed by hydrochloric acid at 150°. It dissolves in boiling water and sodium hydrogen sulphite solution; the latter solution has a blue fluorescence when dilute, but less blue than that of the isomeride. It is insoluble in alcohol, ether, and benzene; its solutions in the alkalis are easily oxidised, and it reduces ammoniacal silver solution. No nitro-derivative was obtained. This acid differs from Witt's amido-α-naphtholsulphonic acid in colour, form, and solubility.

Sulphurous acid is without action on α-nitroso-α-naphthol or ethylnitrolic acid.

The author deduces the following generalisations from the foregoing facts:—

Isonitroso-derivatives of the general formula $HO{\cdot}N{<}^{HR_1}_{R_1}$ form substituted amidosulphonic acids when acted on by sulphurous acid.

Isonitroso-derivatives of the general formula $R_{11}{\cdot}NOH$ may be divided into three classes, according to their behaviour with sodium hydrogen sulphite solution, viz.:—(1) Such as are easily soluble therein; these yield no amidosulphonic acid. (2) Such as are soluble in a boiling solution thereof; these yield amidosulphonic acids, at the same time undergoing a reduction analogous to the conversion of quinone into quinol. (3) Such as are unattacked by the solution thereof. A. G. B.

Aromatic Thiosulphonic Acids. By R. Otto and A. Rössing (*Ber.*, **24**, 3874—3883).—The authors have made experiments with the object of obtaining the tetrathio-compound mentioned in a former paper (Abstr., 1891, 924) in an easier manner, but without success.

A concentrated aqueous solution of potassium toluenethiosulphonate (2 mols.) was allowed to remain in a closed space exposed to the vapours of bromine (2 mols.) at the ordinary temperature until the bromine was absorbed. The product consisted of a mixture of the pentathio- and trithio-compounds with a small quantity of the tetrathio-compound.

When a cold solution of potassium benzenethiosulphonate is mixed with an excess of copper sulphate solution, a crystalline precipitate of a double salt, $3PhSO_2SK,2(PhSO_2S)_2Cu_2,3H_2O$, is obtained, which, when extracted with the usual solvents for polythio-compounds, yields the pentathio- and trithio-compounds. The double salt is stable in air; when heated with potassium hydroxide, it is decomposed with formation of cuprous hydroxide, the latter being quickly converted into copper sulphide, and, when heated alone, it is decomposed above 100°.

When treated with copper sulphate, potassium toluenethiosulphonate behaves in an exactly similar way.

The authors have examined the action of phosphorus pentachloride on the polythio-compounds to determine if a chloride of the formula $PhSO_2{\cdot}SCl$ is formed.

The trithio-compound of benzene, $(PhSO_2)_2S$, when treated with phosphorus pentachloride, yields phosphorus trichloride, sulphur dichloride, and benzenesulphonic chloride. The product of the reaction was boiled with ammonia, when benzenesulphonamide was obtained, but no trace of an amine or salt of the acid $PhSO_2S{\cdot}SH$ could be detected.

The pentathio-compound of toluene, $(C_7H_7SO_2S)_2S$, behaves in a similar way, and yields toluenesulphonic chloride, sulphur dichloride, and phosphorus trichloride.

The authors have also studied the action of phosphorus trichloride and oxychloride on alkali salts of thiosulphonates, in the hope of obtaining chlorides from which, by the action of potash, the thio-acid could be regenerated. The action, however, takes a different course.

Dry potassium benzenethiosulphonate is mixed to a thin paste with phosphorus oxychloride, gently warmed for some hours, then heated to boiling, and the cold product poured into excess of cold, dilute soda solution. A thick, insoluble oil is thus obtained which, when treated with ammonia, partially dissolves, and yields benzenesulphonamide and a very small quantity of benzenethiosulphonate. The product insoluble in ammonia consists of benzene disulphoxide, $PhSO_2{\cdot}S{\cdot}Ph$. It is converted into phenyl bisulphide and potassium benzenesulphinate by boiling with potash. The benzenethiosulphonic acid is thus chiefly converted into the sulphonic chloride. In order to determine if the benzenesulphonic chloride is obtained through the formation of sulphinic acid, dry sodium benzenesulphinate was heated with excess of phosphorus oxychloride, when condensation products of the sulphinic acid were obtained, and only a very slight smell of benzenesulphonic chloride could be detected.

Potassium benzenethiosulphonate and phosphorus trichloride gave benzenesulphonic chloride, only traces of salts of thiosulphonic acid, and phenyl bisulphide. Sodium benzenesulphinate and phosphorus trichloride yielded phenyl bisulphide. E. C. R.

Nitrosulphobenzoic Acid. By Hausser (*Bull. Soc. Chim.* [3], **6**, 391—395).—Hart has obtained salts of the acid

$$SO_3H\cdot C_6H_3(NO_2)\cdot COOH\ [= 2:4:1]$$

by the oxidation of calcium nitrotoluenesulphonate with potassium permanganate. The author oxidises the corresponding potassium salt. 50 grams of potassium nitrotoluenesulphonate, 86 grams of potassium permanganate, and 4500 c.c. of water are heated together on the water-bath for 8—10 hours. The product is cooled, filtered, and concentrated to 500 c.c., when it yields a crop of silky needles. The filtrate is concentrated to 250 c.c.; crystals like those of the first crop first appear; when these begin to appear opaque, the liquid is rapidly filtered, and it then yields the dipotassium salt of nitrosulphobenzoic acid. The yield from the foregoing quantities is 19 grams of nearly pure, dry salt from the third crystallisation. About 15 grams of the original substance is recovered from the first crystallisation, and a further quantity of the dipotassium salt may be obtained from the second crystallisation by treatment with boiling alcohol, which dissolves out the potassium nitrotoluenesulphonate. The total yield of oxidised salt is from 45 to 50 per cent.

Dipotassium nitrosulphobenzoate, $SO_3K\cdot C_6H_3(NO_2)\cdot COOK$, is difficult to purify by crystallisation. The acid salt may easily be purified; it is mixed with a slight excess of potassium carbonate, and the product recrystallised from 60 per cent. alcohol, when it forms large, short prisms free from water. The *monopotassium* salt, $SO_3K\cdot C_6H_3(NO_2)\cdot COOH + H_2O$, is obtained by the action of sulphuric acid on the dipotassium salt, from which it may be distinguished by the longer crystals formed. Excess of sulphuric acid does not decompose this salt. The *lead* salt, $2C_7H_3NSO_7Pb,5H_2O$, is obtained by heating equivalent quantities of the dipotassium salt and normal lead acetate with 15 times their weight of water, filtering rapidly, and allowing to crystallise; it forms short, large prisms. It loses its water with difficulty; but 2 mols. are eliminated on boiling for two hours with water. It is insoluble in cold water; hydrogen sulphide barely produces a coloration in the mother liquors. It has not been obtained free from potassium; several hours boiling with water fails to abstract the whole of this impurity.

The free acid, $SO_3H\cdot C_6H_3(NO_2)\cdot COOH$, is obtained from the lead salt by suspending the latter in 15 times its weight of water and boiling for 20 minutes with the theoretical quantity of sulphuric acid. The product is cooled, filtered, and evaporated down as far as possible. On cooling, it forms a crystalline mass which is treated with a little 95 per cent. alcohol. The alcoholic solution when crystallised over alcohol, gives long, prismatic needles melting at 71—72°; by very slow evaporation, tables are obtained. The acid is very hygroscopic; it loses water in a vacuum over sulphuric acid, when

a form containing $2H_2O$ is obtained, which fuses at 120—125°, loses water, and resolidifies. The anhydrous acid formed fuses at 146°. It crystallises in prismatic bundles. W. T.

Acetylhydrindigotin and Acetylindigotin. By C. Liebermann and D. F. Dickhuth (*Ber.*, **24**, 4130—4136).—*Diacetylindigotin*, $C_6H_4<\overset{CO-}{NAc}>C{:}C<\overset{CO-}{NAc}>C_6H_4$, is readily prepared by the action of nitrous acid on diacetylhydrindigotin in glacial acetic acid; it may also be obtained by the action of oxidising agents, such as chlorine, bromine, chromic anhydride, or nitric acid, on diacetylhydrindigotin, or by the treatment of indigo with acetic chloride in acetic anhydride solution. The compound is very sparingly soluble in organic media, and crystallises from benzene in lustrous, red, tetragonal pyramids which melt at a high temperature. In solution, the compound exhibits characteristic absorption bands between D and E; on treating the acetyl derivative with alkalis, indigo is quantitatively regenerated.

The authors remark on the curious change of colour from blue to red produced by the introduction of two acetyl groups into the indigotin molecule.

Acetylhydrindigotin is insoluble in alkalis; it therefore has the formula $C_6H_4<\overset{CO-}{NAc}>CH{\cdot}CH<\overset{CO-}{NAc}>C_6H_4$, and is termed the ψ-form; an isomeric β-modification,

$$C_6H_4<\overset{C(OH)}{NAc}\!\!>C{\cdot}C<\!\!\overset{C(OH)}{NAc}>C_6H_4,$$

is obtained by cautiously heating acetylindigotin (17 parts) with phenylhydrazine (11 parts) in benzene solution; there is a considerable evolution of nitrogen, and a heavy, colourless, crystalline powder is formed; this is not acted on by nitrous acid; it dissolves in dilute alkalis at ordinary temperatures with formation of indigo, whilst, on boiling with alcohol, acetylindigotin is produced.

Tetracetylhydrindigotin, $C_6H_4<\overset{CAc}{NAc}\!\!>C{\cdot}C<\!\!\overset{CAc}{NAc}>C_6H_4$, is formed by the action of zinc-dust, acetic anhydride, and sodium acetate on diacetylindigotin; the compound is very sparingly soluble, and is deposited from glacial acetic acid as a crystalline powder; it melts at 258° with decomposition, is insoluble in alkalis at ordinary temperatures, but, on boiling, the solution yields indigo.

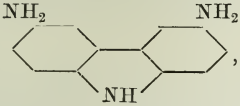
J. B. T.

Synthesis of the Diamidocarbazole obtained from Carbazole. By E. Täuber (*Ber.*, **25**, 128—133).—The diamidocarbazole which is prepared according to a patent of the Bad. Anilin- und Soda-Fabrik, when converted into its tetrazo-derivative, yields with salicylic acid a yellow dye, carbazole-yellow, which dyes unmordanted cotton. From these properties, it was expected that the diamidocarbazole contained both amido-groups in the para-position relatively to the diphenylene

bond. The author has already prepared the diamidocarbazole of this constitution, and has shown that it is not identical with the compound prepared according to the above patent (Abstr., 1891, 227). He has succeeded in synthesising the latter compound as follows:—The acetyl derivative of diorthamidodiphenyl is nitrated, and the product hydrolysed, when a diparanitraniline is obtained; this is reduced to diparaphenylenediamine, and the latter converted into diamidocarbazole by heating with hydrochloric acid.

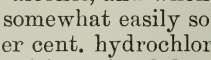
Dimetanitrodiorthamidodiphenyl is obtained as follows:—Pure diorthamidodiphenyl is acetylated by heating it with acetic acid containing one-third its weight of acetic anhydride (*Ber.*, **24**, 199). The dry acetyl compound is dissolved in five times its weight of ice-cold, concentrated sulphuric acid, and finely-powdered potassium nitrate (2 mols.) added to the solution at 10°. When no further reaction can be detected by the thermometer, the mixture is saturated with aqueous potash and warmed on the water-bath. The yellowish-brown powder thus obtained is dissolved in hot hydrochloric acid (20 per cent.), precipitated with water, and crystallised from a mixture of phenol and alcohol. It crystallises in small, golden-yellow prisms having a violet reflex, melts at about 285°, but darkens at 250°, and becomes tarry at 280°. It is insoluble in ether, benzene, toluene, and light petroleum, very sparingly soluble in water, chloroform, and alcohol, easily so in boiling phenol, and has very feeble basic properties.

Diparaphenylenediamine, $C_{12}H_6(NH_2)_4$ [= 2 : 5 : 2′ : 5′], is obtained in the form of its hydrochloride by reducing the preceding compound with tin and hydrochloric acid. The base is precipitated from the solution of its easily soluble hydrochloride by strong aqueous potash; by ammonia or dilute potash, it is not precipitated. It crystallises from boiling toluene in aggregates of colourless needles, melts at 168°, is easily soluble in water, alcohol, and chloroform, sparingly so in boiling benzene, toluene, and ether, and insoluble in cold benzene, toluene, and light petroleum. Both the hydrochloride and the sulphate are easily soluble. The constitution of the base is deduced from the following observations:—It does not react with orthodiketones such as dibenzoyl and dihydroxytartaric acid; when diazotised with nitrous acid, it does not yield a dye; hence the amido-groups are not in the ortho- or para-position relatively to each other. It gives the indamine and indophenole reactions characteristic of paradiamines.

Diamidocarbazole,  , is obtained by heating diparaphenylenediamine for 10 hours in a sealed tube with five times the quantity of hydrochloric acid (15—20 per cent.) at 180—190°. The product is diluted with water, warmed with a little stannous chloride, the tin precipitated with hydrogen sulphide, the filtered, colourless solution evaporated until it contains 3—5 per cent., and mixed then with an equal volume of hydrochloric acid (25 per cent.). On cooling, the hydrochloride separates in tufts of long, white, lustrous needles. The free base is obtained in silvery leaflets by precipitating

a hot solution of the hydrochloride with ammonia; it darkens at 260°, does not melt at 290°, is insoluble in ether, almost so in cold water, sparingly soluble in hot water, somewhat sparingly so in benzene, toluene, and alcohol, and when damp is acted on by the air. The *hydrochloride* is somewhat easily soluble in water, and quite insoluble in cold 10 per cent. hydrochloric acid. Tho *sulphate* is not precipitated by the addition of sulphuric acid to a solution of the hydrochloride unless the latter is concentrated, but separates in beautiful needles on adding sodium sulphate to very dilute solutions, and is easily soluble in dilute hydrochloric acid, sparingly so in water.

E. C. R.

Diphenylenazone. By E. Täuber (*Ber.*, **24**, 3883—3886; see also this vol., p. 183).—Diphenylenazone,  , sublimes with difficulty in bright, greenish-yellow needles, melts at 156°, and is not volatile with steam. The *aurochloride* and *platinochloride* are very sparingly soluble in water, and crystallise in yellow needles. The *chromate* is obtained in beautiful, red needles by adding a hot solution of chromic acid to a hot solution of the phenazone in dilute sulphuric acid, and is very sparingly soluble. The *picrate* is obtained by mixing very dilute, hot benzene solutions of the two components; on cooling, it separates in feathery, brown needles, is very sparingly soluble, coagulates at 190°, and melts at 194°. The *hydrochloride* is obtained by adding a hot saturated solution of the phenazone to excess of hydrochloric acid and allowing the mixture to cool slowly. It crystallises in flat prisms, having a bronze lustre, and can be dried in the air without decomposing, but in a vacuum, or on gently warming, it loses hydrogen chloride; it is also decomposed by water. Diphenylenazone is extremely stable towards oxidising agents. When treated with zinc and hydrochloric acid or tin and hydrochloric acid, the azo-group is converted into the hydrazone group. Stannous chloride and alcoholic ammonium sulphide are without action on it. When treated with bromine in benzene solution, it yields a brick-red, crystalline precipitate, which turns yellow on drying.

It is distinguished from phenazine by the following properties, besides those given above:—It dissolves in concentrated sulphuric acid with a sulphur-yellow coloration, and its hydrazone gives the same colour; whilst phenazine gives a blood-red and its hydrazone a green coloration.

E. C. R.

Benzaldiphenylmaleïde and its Derivatives. By G. Cohn (*Ber.*, **24**, 3854—3874).—The author, in conjunction with Gabriel, has shown that benzaldiphenylmaleïde is formed by the action of diphenylmaleïc anhydride on phenylacetic acid with elimination of water and carbonic anhydride (this vol., p. 178).

Paraxylaldiphenylmaleïde, $\begin{matrix}CPh{:}CPh\\ |\\ CO\text{---}O\end{matrix}>C{:}CH\cdot C_7H_7$, is obtained in the same way by the condensation of paratolylacetic acid and diphenylmaleïc anhydride. It crystallises from acetic acid in yellow

needles, melts at 165°, and is more easily soluble in alcohol and acetic acid than benzaldiphenylmaleïde.

Dibromobenzyldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ \text{CO}\text{---}\text{O}\end{matrix}\!>\!\text{CHPhBr}$, is obtained by adding bromine (2 c.c.) to benzaldiphenylmaleïde (5 grams) suspended in chloroform (50 c.c.), and allowing the mixture to evaporate in a dish for 5—10 hours in a cold place. It is purified by washing with acetone and then dissolving in chloroform and precipitating with acetone. It forms large, hard, rhombic crystals when allowed to crystallise slowly, melts at 154° with evolution of gas, and is easily soluble in hot benzene, chloroform, and acetic acid, very sparingly so in hot acetone.

Bromobenzaldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ \text{CO}\text{---}\text{O}\end{matrix}\!>\!\text{C:CPhBr}$, is obtained by heating the preceding compound at 155—160°; it crystallises from acetone in well-formed, measurable crystals, belonging to the rhombohedral system, and melts at 165°.

Hydroxybenzaldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ \text{CO}\text{---}\text{O}\end{matrix}\!>\!\text{C:Ph·OH}$, is obtained by dissolving the finely-powdered dibromo-compound in alcoholic potash and boiling the solution for 5—10 minutes; the product is poured into water, the alcohol distilled off, and the cold solution precipitated with hydrochloric acid. It crystallises in long, yellow needles, melts at 205°, but sinters at a somewhat lower temperature, is insoluble in ammonia, easily soluble in potassium hydroxide, and is quantitatively reprecipitated by carbonic anhydride.

Benzylhydroxydiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ \text{CO}\text{---}\text{O}\end{matrix}\!>\!\text{C(OH)·CH}_2\text{Ph}$, is obtained by warming benzaldiphenylmaleïde (5 grams) with concentrated potassium hydroxide (25 grams) for some hours on the water-bath or by boiling the mixture until the compound has melted to a brown oil. The oil, which is the potassium salt of the new compound, is dissolved in hot water; the cold solution precipitated with hydrochloric acid, and the precipitate crystallised from dilute alcohol or dissolved in benzene and precipitated with light petroleum. The potassium salt can easily be obtained pure by allowing the finely-powdered maleïde to remain with a molecular proportion of absolute alcoholic potash for 24 hours with frequent shaking; the yield is, however, not so good as by the first method. It sinters at 170°, melts at 183—185°, is easily soluble in alcohol, less so in benzene, very slightly so in light petroleum, and insoluble in ammonia, but easily soluble in sodium hydroxide. It is precipitated from solution by excess of soda, and from alcoholic solution by carbonic anhydride. It does not yield an acetyl derivative or methyl ether, but, under these experimental conditions, is reconverted into benzaldiphenylmaleïde.

β-Phenacetyl-αβ-diphenylacrylamide,

$$\text{NH}_2\text{·CO·CPh:CPh·CO·CH}_2\text{Ph},$$

is obtained by heating benzaldiphenylmaleïde (5 grams) with 10 per cent. alcoholic ammonia (20 c.c.) at 100° for four hours. It is purified

by crystallisation from alcohol, forms microscopic, rhombic plates, and melts at 203—204°.

Benzaldiphenylmaleïmidine, $\begin{matrix}\text{CPh:CPh}\\ \text{CO—NH}\end{matrix}\!>\!\text{C:CHPh}$, is obtained by adding the above amide in fine powder to boiling acetic acid. It is purified by crystallisation from acetic acid, melts at 241—242°, and is very sparingly soluble in boiling alcohol.

Bromobenzaldiphenylmaleïmidine, $\begin{matrix}\text{CPh:CPh}\\ \text{CO—NH}\end{matrix}\!>\!\text{C:CPhBr}$, is obtained by adding bromine as long as it is absorbed to the preceding compound suspended in chloroform. It is purified in the same way as bromobenzaldiphenylmaleïde, crystallises in white, felted needles, and melts at 213—214°.

β-Phenacetyl-αβ-diphenylacrylethylamide,

$$\text{NHEt·CO·CPh:CPh·CO·CH}_2\text{Ph},$$

is obtained by the action of ethylamine on the maleïde in the same way as the above amide is by the action of ammonia. It crystallises from benzene in aggregates of slender, white needles, and melts at 172—173°. When boiled with acetic acid, it is converted into *benzaldiphenylmaleïnethylimidine*. The latter crystallises from alcohol, melts at 144—146°, and is easily soluble in most organic solvents.

Benzyldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ \text{CO —— O}\end{matrix}\!>\!\text{CH·CH}_2\text{Ph}$, is obtained by gradually adding a mixture of benzaldiphenylmaleïde (10 grams) and amorphous phosphorus (5 grams) to 50 c.c. of boiling hydriodic acid (sp. gr. = 1·7—1·96). After heating for some time in a reflux apparatus, a brown oil is obtained floating on the liquid; the mixture is then boiled for 1—2 hours, and, on cooling, the oil solidifies. It is treated with very dilute sodium hydrogen sulphite, dissolved in alcohol, and sulphurous anhydride passed through the solution, filtered, and the alcohol allowed to evaporate. It forms small, hard, white crystals, melts at 127—128°, is easily soluble in chloroform, alcohol, and benzene, sparingly so in light petroleum. It does not give an additive compound with bromine, and is insoluble both in ammonia and aqueous potassium hydroxide.

αβδ-Triphenyl-γ-hydroxypropylidenacetic acid,

$$\text{COOH·CPh:CPh·CH(OH):CH}_2\text{Ph},$$

is obtained by dissolving the preceding compound in warm alcoholic potash. It crystallises from dilute alcohol or acetic acid in compact needles, sinters at 120—140°, melts at 173—174°, is easily soluble in ammonia and dilute sodium hydroxide and carbonate, and is precipitated as sodium salt by excess of sodium hydroxide or carbonate. The *silver* salt is obtained in white flocks on adding silver nitrate to a faintly ammoniacal solution of the acid. No definite compound was obtained from it by heating. It is converted into benzyldiphenylmaleïde by the action of phosphorus oxychloride.

Benzyldiphenylmaleïmidine, $\begin{matrix}\text{CCPh:Ph}\\ \text{CO—NH}\end{matrix}\!>\!\text{CH·CH}_2\text{Ph}$, is obtained by

heating benzyldiphenylmaleïde with alcoholic ammonia in a sealed tube at 180° for seven hours. If the tube is slowly cooled, it crystallises in aggregates of rhombic plates which are measurable. It is purified by crystallisation from dilute alcohol, melts at 169—170°, dissolves in chloroform, and is reprecipitated on the addition of ether. The *nitrosamine* is obtained by suspending the maleïmidine in benzene and passing nitrous anhydride into the mixture until it dissolves; the benzene is allowed to evaporate off and the product crystallised from methyl and then from ethyl alcohol. It melts at 135—136°, gives Liebermann's reaction, is somewhat easily soluble in alcohol, and yields benzaldiphenylmaleïmidine with evolution of nitrous oxide when boiled with potassium hydroxide.

If benzyldiphenylmaleïmidine is warmed with dry phosphorus oxychloride, it is converted into a compound which dissolves with a deep-violet colour in alcohol, and is obtained as a brownish-red base on precipitating the hot alcoholic solution with ammonia. The base is sparingly soluble in alcohol, does not dye either wool or silk, gives a brown solution with concentrated sulphuric acid and forms salts, which are decomposed by water. It is probably analogous to the compound obtained by Gabriel (*Ber.*, **20**, 2865) from benzylphthalimidine.

αβδ-Triphenyl-γ-hydroxypropylidenacetethylamide,

$$NHEt\cdot CO\cdot CPh{:}CPh\cdot CH(OH)\cdot CH_2Ph,$$

is obtained by heating benzyldiphenylmaleïde with 10 per cent. alcoholic ethylamine for 3—4 hours at 180°; it crystallises from alcohol in white needles, and melts at 194—196°.

Benzyldiphenylmaleïnethylimidine, $\begin{matrix} CPh{:}CPh \\ | \\ CO-NEt \end{matrix}\!\!>\!CH\cdot CH_2Ph$, is obtained in small quantities by boiling the preceding compound with acetic acid. It is, however, best obtained by reducing the corresponding benzal derivative with hydriodic acid and phosphorus. It crystallises from alcohol in pale-yellow, nodular crystals and melts at 125°. The pure substance gives no coloured product with phosphorus oxychloride; when impure, it yields a compound which dissolves in alcohol with a blue coloration, and on precipitation with ammonia it yields a yellow base.

Hydroxynitrobenzyldiphenylmaleïde, $\begin{matrix} CPh{:}CPh \\ | \\ CO\!-\!\!-\!\!-\!O \end{matrix}\!\!>\!C(OH)\cdot CHPh\cdot NO_2$, is obtained by treating benzaldiphenylmaleïde (5 grams) suspended in benzene (30 c.c.) with a stream of nitrous anhydride, produced by the action of arsenious anhydride on nitric acid (sp. gr. = 1·33). The temperature must not be allowed to rise above 60°, and care must be taken that all the maleïde dissolves. After a time, a white, crystalline compound separates from the dark-green solution. It is collected, dried on a porous plate, and crystallised from ether. The yield amounts to 35 per cent. A somewhat larger yield is obtained by suspending the lactone in 10 times the quantity of benzene, adding two to three times the theoretical quantity of nitrogen tetroxide, and allowing the mixture to remain. The best yield, about 65 per

cent., is obtained by nitrating in five times the volume of glacial acetic acid, to which a few drops of water have been added. It melts at 123—125°, is sparingly soluble in cold benzene and acetic acid, easily so in ether, is very unstable, and is decomposed by hot acetic acid and alcohol, by prolonged boiling with benzene, or by heating with water. When subjected to steam distillation, it is decomposed into phenylnitromethane and diphenylmaleïc anhydride. The *acetyl derivative*, $C_{23}H_{16}NO_5Ac$, is obtained on heating it in a sealed tube with four times the quantity of acetic chloride for four hours at 100°; it crystallises from alcohol in rhombic, six-sided leaflets, melts at 166°, sinters about 10° lower, and explodes when strongly heated.

Dinitrobenzyldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ |\\ \text{CO}\text{---}\text{O}\end{matrix}>\text{C}(\text{NO}_2)\cdot\text{CHPh}\cdot\text{NO}_2$, is obtained by evaporating the green benzene solution obtained in the preparation of the preceding compound at about 30°, and purifying the semi-solid mass thus obtained by washing it with ether and precipitating the chloroform solution with ether. It forms a lustrous, crystalline powder, melts at 146° with decomposition, and is easily soluble in chloroform and acetic acid, sparingly so in ether, and only very sparingly in alcohol, which decomposes it. It is also obtained by nitrating benzaldiphenylmaleïde in boiling acetic acid.

Nitrobenzaldiphenylmaleïde, $\begin{matrix}\text{CPh:CPh}\\ |\\ \text{CO}\text{---}\text{O}\end{matrix}>\text{C:CPh}\cdot\text{NO}_2$, is obtained by boiling the preceding compound with acetic acid or alcohol or by heating it at its fusion point until evolution of nitrous fumes ceases. It crystallises in yellow leaflets, melts at 175—177°, is easily soluble in hot chloroform, somewhat sparingly so in ether and alcohol, begins to decompose at 190°, and explodes violently when heated in a test tube, yielding phenyl isocyanate and diphenylmaleïc anhydride. When dissolved in warm alcoholic potash, it is converted into the above hydroxynitro-compound. When reduced with hydriodic acid and phosphorus, it is converted into a compound which the author believes to be *isobenzaldiphenylmaleïde*, $\begin{matrix}\text{CPh:CPh}\cdot\text{CH}\\ |\quad\quad\quad\|\\ \text{CO}\text{---}\text{O}\cdot\text{CPh}\end{matrix}$, melting at 118°. If the latter is heated with alcoholic ammonia for some time at 100°, it yields a compound which crystallises in long, white needles, melts above 260°, and is very sparingly soluble in alcohol; the author believes this to be *isobenzaldiphenylmaleïmidine*, $\begin{matrix}\text{CPh:CPh}\cdot\text{CH}\\ |\quad\quad\quad\|\\ \text{CO}\text{–NH}\text{–}\text{CPh}\end{matrix}$, and has obtained triphenylpyridine from it by treatment with phosphorus oxychloride and subsequent reduction.

Hydroxynitrobenzyldiphenylmaleïmidine,

$$\begin{matrix}\text{CPh:CPh}\\ |\\ \text{CO}\text{—}\text{NH}\end{matrix}>\text{C}(\text{OH})\cdot\text{CHPh}\cdot\text{NO}_2,$$

is obtained as a crystalline powder by passing nitrous anhydride into an ice-cold mixture of benzaldiphenylmaleïmidine (5 grams) suspended in 20 c.c. of acetic acid and $\frac{1}{2}$ c.c. of water. It is collected on an asbestos filter, well washed with acetic acid, and dried on a

porcelain plate and then in a vacuum. It is also obtained in small quantity by nitrating in chloroform solution. By slowly evaporating the ethereal solution, it is obtained in stellate groups of large crystals, is sparingly soluble in cold acetic acid and benzene, easily so in hot chloroform and ether, but insoluble in light petroleum; it is decomposed by boiling with benzene and alcohol, and is very unstable, turning yellow on exposure to air and also in a vacuum. When subjected to steam distillation, it is decomposed into phenylnitromethane and diphenylmaleïc anhydride.

Nitrobenzaldiphenylmaleïmidine, $\begin{matrix}\text{CPh:CPh}\\ \text{CO—NH}\end{matrix}\!\!>\!\text{C:CPh·NO}_2$, is obtained by allowing the preceding compound to remain 24 hours with acetic chloride or by boiling it for a short time with this reagent. It crystallises in yellow needles, melts at 201—202°, dissolves in concentrated sulphuric acid with a red coloration, which changes to yellow on gently heating, and explodes about 260° with formation of phenyl isocyanate and diphenylmaleïc imide. When treated with alcoholic potash, it is converted into a potassium salt, sparingly soluble in alcohol, and, on adding water and distilling off the alcohol and then adding hydrochloric acid to the cold solution, a yellow precipitate is obtained which, on boiling, yields phenylnitromethane and diphenylmaleïc anhydride.

By nitrating benzaldiphenylmaleïmidine in benzene, a product is obtained, together with nitrobenzaldiphenylmaleïmidine, which crystallises in beautiful, yellow, pointed forms built up of thin, quadratic plates. It gave, on analysis, numbers agreeing with the formula $C_{30}H_{22}N_2O_5$, melts at 173°, decomposes at 195—198°, and behaves towards concentrated sulphuric acid and soda like nitrobenzaldiphenylmaleïmidine.

When benzaldiphenylmaleïnethylimidine is nitrated in benzene, it yields a compound of the formula $C_{18}H_{14}N_2O_4$, which crystallises from alcohol in beautiful, bright-yellow plates, melts at 151°, and sublimes without decomposition. The author believes it to be a nitro-derivative of the unknown diphenylmaleïnethylimide, $C_{16}H_{10}O_2$:N·Et.

E. C. R.

Influence of Substituting Radicles on the Configuration of Aromatic Ketoximes. By A. W. Smith (*Ber.*, **24**, 4025—4058; compare Hantzsch, this vol., p. 426).—The author has prepared the oximes of a great number of benzophenone derivatives in order to study the influence of the substituting groups, both with regard to their nature and position, on the properties and stability of the two theoretically possible stereoisomeric modifications.

The alkyl derivatives of benzophenone were prepared by treating a hydrocarbon, such as propylbenzene, with an acid chloride, such as benzoic chloride, in carbon bisulphide solution in presence of aluminium chloride; the yield of the pure ketone usually amounted to 60 to 80 per cent. of the theoretical. The oximes were prepared by Auwers' method, and in cases where two stereoisomeric modifications were formed, their separation was effected by fractional precipitation from acetic acid or from alcohol. The configuration of the oximes was determined by treating the compound with phosphorus penta-

chloride and water successively, as described by Hantzsch (Abstr., 1891, 445); under these conditions, the stable isomeride is completely converted into the corresponding anilide, the labile modification yielding, as a rule, a mixture of two structurally isomeric anilides. When necessary for identification, the anilides were converted into the corresponding acids by treatment with concentrated hydrochloric acid at about 150°, the base produced at the same time being, as a rule, identified by means of its acetyl derivative; these experiments are not described in this abstract, except in cases where new compounds were obtained.

Antiparethylbenzophenone oxime, $C_6H_4Et\cdot\overset{N\cdot OH}{\overset{\|}{C}}\cdot Ph$, is obtained, together with an approximately equal quantity of the isomeric synoxime, when parethylbenzophenone (b. p. 330—332°) is treated with hydroxylamine and soda in dilute alcoholic solution; it crystallises from alcohol in short, thick, monoclinic prisms, melts at 142°, and is readily soluble in ether and glacial acetic acid, but more sparingly in cold alcohol and benzene, almost insoluble in cold light petroleum, and insoluble in water. The *acetyl* derivative crystallises from alcohol in colourless, monoclinic prisms, melts at 95°, and is reconverted into the oxime (m. p. 142°) on treatment with soda. When the antioxime is heated at 120° for 20 hours with soda and hydroxylamine, it is almost completely converted into the synoxime.

Parethylbenzanilide, $C_6H_4Et\cdot CO\cdot NHPh$, prepared by treating the antioxime with phosphorus pentachloride and water successively, crystallises from alcohol in lustrous needles, melts at 121°, and is readily soluble in alcohol and ether, but insoluble in water; no other anilide is produced from the antioxime.

Synparethylbenzophenone oxime, $C_6H_4Et\cdot\overset{OH\cdot N}{\overset{\|}{C}}\cdot Ph$, crystallises from alcohol in long, thin needles, melts at 108°, dissolves freely in ether and glacial acetic acid, and is much more readily soluble in alcohol and dilute acetic acid than the stereoisomeride. The *acetyl* derivative, prepared in the cold, is a thick oil, and is reconverted into the synoxime by treatment with cold soda; when warmed with alcohol, it is completely converted into the acetyl derivative of the antioxime. When the synoxime is treated with phosphorus pentachloride and water successively, it is almost entirely converted into benzoylparethylanilide, only traces, if any, of parethylbenzanilide being formed.

Parapropylbenzophenone, $C_6H_4Pr\cdot COPh$, is a thick, yellowish liquid boiling at 203° under a pressure of 180 mm.; on treatment with hydroxylamine, it yields two oximes.

Antipropylbenzophenone oxime, $C_{16}H_{17}NO$, crystallises from dilute alcohol or acetic acid in slender needles melting at 104°; it is not converted into the synoxime by treatment with acids, or with soda and hydroxylamine. The *acetyl* derivative separates from alcohol in crystals, melts at 66°, and is reconverted into the antioxime on hydrolysis with soda. The *anilide*, $NHPh\cdot CO\cdot C_6H_4Pr$, is formed when the antioxime is treated with phosphorus pentachloride and

water successively; it crystallises from alcohol in flat prisms, melts at 138°, and is only sparingly soluble in alcohol, ether, and benzene.

Synpropylbenzophenone oxime, $C_{16}H_{17}NO$, crystallises from alcohol in long, lustrous prisms, melts at 130°, and is more sparingly soluble in alcohol than the isomeride, but almost as readily soluble as the latter in ether and glacial acetic acid. The *acetyl* derivative crystallises in slender needles, melts at 116°, and is reconverted into the synoxime by alkalis; when warmed with acetic chloride, it is transformed into the acetyl derivative of the antioxime. When the synoxime is treated with phosphorus pentachloride and water successively, it yields parapropylbenzanilide, $C_6H_4Pr{\cdot}NH{\cdot}COPh$.

Parisopropylbenzophenone, $C_6H_4Pr^{\beta}{\cdot}COPh$, is a thick oil boiling at 343° under a pressure of 738 mm.; when treated with hydroxylamine, it gives two oximes.

Antiparisopropylbenzophenone oxime, $C_{16}H_{17}NO$, crystallises from alcohol or glacial acetic acid in long, monoclinic prisms, melts at 132°, and is not changed by boiling soda even in presence of hydroxlamine. The *acetyl* derivative crystallises from alcohol in short, monoclinic prisms, melts at 90°, is readily soluble in alcohol and ether, and is reconverted into the antioxime on hydrolysis with sodium carbonate.

Cuminylanilide, $NHPh{\cdot}CO{\cdot}C_6H_4Pr^{\beta}$, is formed when the antioxime is treated with phosphorus pentachloride and water successively; it crystallises from alcohol in long, lustrous needles, melts at 159°, and is readily soluble in alcohol, but more sparingly in ether and benzene.

Synparisopropylbenzophenone oxime, $C_{16}H_{17}NO$, crystallises from alcohol, in which it is much more readily soluble than the isomeride, in long needles melting at 106°. The *acetyl* derivative is an oil, and is reconverted into the synoxime on hydrolysis with sodium carbonate; when heated alone, or with alcohol, it is transformed into the acetyl derivative of the antioxime. When the synoxime is treated with phosphorus pentachloride and water successively, it yields a mixture of cuminylanilide and benzoylcuminide; when treated with hydrogen chloride in ethereal solution, or with acetic acid, it is completely transformed into the antioxime.

Paramidobenzophenone combines with hydroxylamine, yielding two *oximes* of the composition $C_{13}H_{12}N_2O$; the one, probably the anti-oxime, melts at 168°, crystallises from alcohol in long, monoclinic prisms, and is only sparingly soluble in alcohol and benzene, but more readily in ether and glacial acetic acid; the other oxime, probably the syn-isomeride, crystallises in slender, colourless needles, melts at 126°, and is more readily soluble in alcohol than the compound of higher melting point.

Parahydroxybenzophenone is best obtained by heating paramethoxybenzophenone at 145—150° for 3—4 hours with an aqueous solution of hydrogen choride, saturated at 0°; when boiled with hydroxylamine and potash in alcoholic solution for 4—5 hours, it yields two oximes.

Antiparahydroxybenzophenone oxime, $C_{13}H_{11}NO_2$, crystallises from dilute acetic acid in slender, monoclinic prisms, melts at 125°, and is

readily soluble in ether and alcohol, but rather more sparingly in glacial acetic acid, benzene, and chloroform, and very sparingly in water; it dissolves in alkalis and in concentrated acids. The *acetyl* derivative crystallises in prisms, melts at 141° with decomposition, and is readily soluble in alcohol, but more sparingly in ether and benzene; on hydrolysis with sodium carbonate, it is reconverted into the antioxime. When the oxime is treated with phosphorus pentachloride in the usual manner, it yields parahydroxybenzanilide and smaller quantities of other products; on prolonged boiling with alkali, it is quantitatively converted into the synoxime.

Synparahydroxybenzophenone oxime, $C_{13}H_{11}NO_2$, crystallises in needles, melts at 81°, and is very readily converted into the antioxime when heated alone for a short time at about 80°, or when treated with hydrogen chloride in ethereal solution; it reacts with acetic chloride and with acetic anhydride in the cold, yielding a syrup, which, on hydrolysis with sodium carbonate, gives a mixture of the anti- and syn-oximes, and which, when heated alone, is completely transformed into the acetyl derivative of the antioxime. When the synoxime is treated with phosphorus pentachloride and water successively, it yields benzoylparamidophenol (m. p. 205—207°) and smaller quantities of other products.

Metahydroxybenzophenone, $C_{13}H_{10}O_2$, can be prepared by diazotising the corresponding metamido-compound; it crystallises in lustrous plates, melts at 116°, and is very readily soluble in alcohol and ether, but only sparingly in hot, and almost insoluble in cold, water; when boiled with hydroxylamine in alcoholic solution, it yields the synoxime as sole product.

Synmetahydroxybenzophenone oxime, $C_{13}H_{11}NO_2$, separates from benzene in crystals, melts at 75—76°, and is converted into the antioxime when heated at its melting point, or when treated with hydrogen chloride at the ordinary temperature.

Antimetahydroxybenzophenone oxime, $C_{13}H_{11}NO_2$, prepared by gradually heating the synoxime to 80—90°, crystallises in slender needles, melts at 126°, and is very readily soluble in alcohol, chloroform, and ether, but more sparingly in benzene; it is converted into the synoxime by boiling potash.

Antiorthotolylphenylketoxime, $C_{14}H_{13}NO$, is obtained when orthotolyl phenyl ketone is treated with hydroxylamine and potash in alcoholic solution at the ordinary temperature; it melts at 105°, and, on treatment with phosphorus pentachloride in the usual manner, it yields *orthotoluylanilide*, $C_6H_4Me{\cdot}CO{\cdot}NHPh$ (m. p. 125°). The *acetyl* derivative is a thick syrup, which, on hydrolysis with sodium carbonate, is reconverted into the antioxime.

Synorthotolylphenylketoxime, $C_{14}H_{13}NO$, is formed in small quantities (about 20 per cent.), together with the antioxime (about 80 per cent.), when the ketone is boiled with an alcoholic solution of hydroxylamine and potash for 10 hours; it melts at 69°.

Antixylylphenylketoxime, $C_{15}H_{15}NO$, is formed, together with a small quantity of the synoxime, when xylyl phenyl ketone [$CO : Me_2 = 1 : 2 : 4$] is treated with hydroxylamine and potash in alcoholic solution at the ordinary temperature; if the crude product be warmed

with glacial acetic acid for a long time, the synoxime is completely transformed into the isomeride. It crystallises in flat prisms or plates, melts at 126°, and is very readily soluble in glacial acetic acid, ether, and alcohol, but more sparingly in benzene, and almost insoluble in water. The *acetyl* derivative crystallises in long, flat prisms, melts at 91°, and, on hydrolysis, is reconverted into the antioxime. When the oxime is treated with phosphorus pentachloride and water successively, it yields metaxyloylanilide (m. p. 139°).

Synxylylphenylketoxime, $C_{15}H_{15}NO$, crystallises from alcohol in short prisms, melts at 152°, and is more sparingly soluble in alcohol than the antioxime. The *acetyl* derivative, prepared in the cold, separates from alcohol in crystals melting at 103°, and, when hydrolysed in the cold, is reconverted into the synoxime; it is readily converted into the isomeride on warming, and, on prolonged treatment with acetic chloride at the ordinary temperature, it yields a mixture of the anti-acetyl derivative and *benzoylxylide*, $COPh{\cdot}NH{\cdot}C_6H_3Me_2$. The last-named compound is also produced almost exclusively when the synoxime is treated with phosphorus pentachloride in the usual manner at −20°, but when the reaction is carried out at the ordinary temperature, a mixture of benzoylxylide and xyloylanilide is obtained.

Xylyl orthotolyl ketone, $C_6H_3\overset{2,4}{Me_2}{\cdot}\overset{1}{CO}{\cdot}C_6H_4\overset{2}{Me}$, prepared from orthotoluic chloride and metaxylene, is a thick, yellowish oil boiling at 329—330° under a pressure of 728 mm.; it does not combine with hydroxylamine when boiled therewith in neutral, acid, or alkaline solution, but when the solution (acid or alkaline) is heated at 120° in sealed tubes for five hours, 50—60 per cent. of the ketone is converted into a mixture of xyloyltoluide and *orthotoluylxylide;* the last-named compound crystallises from alcohol in small, seemingly orthorhombic plates melting at 165°.

Mesityl phenyl ketone is not acted on by hydroxylamine even at 120°.

The author draws the following conclusions from the results of the above experiments:—An alkyl group has a repellent action on the hydroxyl group of the hydroxylamine molecule, in consequence of which the anti- is more stable than the syn-oxime; as the molecular weight of the alkyl group increases, its influence decreases, as is shown by the relative stability of the synoximes of methyl-, ethyl-, and propyl-benzophenone. The intensity of the repellent action varies with the constitution of the alcohol radicle, a normal radicle having less influence than an iso-radicle. Halogens and hydroxy- and amido-groups exert an influence similar to that of alcohol radicles, that is to say, the syn- are less stable than the anti-oximes. The terms stable and labile, as applied to oximes, are, however, purely relative, as a change of conditions or of chemical influences may reverse the relative stability; in the case of halogen derivatives of benzophenone, for example, one modification of the oxime is relatively the more stable in presence of acids, the other in presence of alkalis. The influence of various groups on the configuration of aromatic oximes is practically the same, whether the group be in the meta- or the para-

position to the carbon atom of the carbonyl radicle, and is only very slight in either case; when, however, the substituting group is in the ortho-position, its influence is very considerable, the syn- being far less stable than the anti-oxime. F. S. K.

Indulines. By E. Istel (*Chem. Zeit.*, **14**, 1535).—A blue dye, soluble in water, has been mentioned as being present among the products of the action of aniline hydrochloride on amidoazobenzene hydrochloride in concentrated aqueous solution. The author has studied this substance together with other compounds which are likewise formed at the same time.

If 2·5 parts of aniline hydrochloride and 1 part of amidoazobenzene hydrochloride are digested with 6 parts of water, at a temperature of 70—80°, the colour, at first yellow, changes to violet, and later to blue. After 24 hours, the strength of the coloration does not increase. Water is then added, the insoluble portion filtered off, and the blue dye precipitated with salt. Obtained in this way, it is a brown powder, only sparingly soluble in cold water, but readily in hot water, forming a blue solution with reddish-brown fluorescence. It dissolves in alcohol, forming a blue solution, but it is insoluble in ether. Addition of concentrated hydrochloric or sulphuric acid to the aqueous solution causes a reddish coloration, but the dye dissolves in the concentrated acid with blue coloration. Soda precipitates the dye as a blackish-brown powder. Zinc reduces it. Unbleached cotton is dyed a beautiful blue, as also are wool and silk, the former with a somewhat reddish tinge. The author considers the substance an induline, but different from that described in D.R.P. 50,534 (*Chem. Zeit.*, **14**, 353).

The material from which the above substance was dissolved out by water was now extracted with alcohol, by means of which another substance, soluble in alcohol with blue coloration, was separated. It forms a blackish-brown powder, and is a beautiful, grey-coloured nigrosine. In addition, azophenine was found as a product of the reaction, although this was hardly to be expected at so low a temperature. J. W. L.

Methylnaphthylenes. By H. Wichelhaus (*Ber.*, **24**, 3918—3921).—The methylnaphthalenes, as obtained from coal-tar oil by the usual process of distillation, or of freezing-out, are always contaminated with diphenyl. They may, however, be obtained pure in the following manner :—The higher boiling portion of the oil is cooled in a special apparatus, described in the paper, first to 0°, then to −21°, and finally to −36°, the solid substance which separates being drained, at each successive temperature, from the still liquid portion by means of the pump. The solid and liquid hydrocarbons thus obtained are separately dissolved in alcohol, and treated with an alcoholic solution of picric acid; the picrate which separates out is washed with alcohol and decomposed with ammonia, and the hydrocarbon distilled over with steam.

α-Methylnaphthalene is a colourless, fluorescent oil, boiling at

240—242°, and remaining liquid at −36° ; it has a sp. gr. = 1·013 at 19°, and its picrate melts at 117°.

β-Methylnaphthalene forms white, lustrous plates, soluble in alcohol, α-methylnaphthylene, &c.; it melts at 37—38°, and boils at 240—241° ; its picrate melts at 115°. It may also be obtained from the coal-tar oil by cooling it to −15°, treating the solid substance which then separates with picric acid, and decomposing the picrate with an insufficient quantity of ammonia. This decomposes the α- in preference to the β-picrate ; the latter is freed from ammonium picrate by washing with water, and from α-methylnaphthalene by pressing on unglazed porcelain ; it is then decomposed with ammonia, and the resulting β-methylnaphthalene distilled over with steam, rendered solid by cooling to 0°, and recrystallised from alcohol.

C. F. B.

Action of Chlorine and of Nitric Acid on the Methylnaphthalenes. By O. Scherler (*Ber.*, **25**, 3921—3932).—When chlorine is passed at the ordinary temperature over β-methylnaphthalene, it liquefies, chlorine is absorbed, and some hydrogen chloride is evolved. The product is washed with water, dried, extracted with light petroleum, and crystallised from ether. *Chloro-β-methylnaphthalene tetrachloride*, $C_{10}H_6MeCl,Cl_4$, is thus obtained in lustrous, colourless, monosymmetric prisms or tables ; $a : b : c = 1·3696 : 1 : 1·4852$; $\beta = 81° 47'$; it melts at 148°, and dissolves readily in chloroform, ether, and acetic acid, sparingly in alcohol, not at all in light petroleum. That it has the formula given above appears from the fact that when treated with alcoholic potash it loses hydrochloric acid, and forms *trichloro-β-methylnaphthalene*, $C_{10}H_4MeCl_3$. This crystallises from alcohol in small, white needles, melts at 182°, and dissolves readily in ether, chloroform, acetic acid, and hot alcohol, less readily in cold alcohol. When boiled with dilute nitric acid, it yields phthalic anhydride ; hence the three chlorine atoms must be contained in the same ring as the methyl group. When the tetrachloride in acetic acid solution is treated with just sufficient permanganate to oxidise the methyl group, small needles melting at 70° are obtained ; these appear to be *trichloronaphthoic acid*, $C_{10}H_4Cl_3·COOH$.

When the crude product of the action of chlorine on β-methylnaphthalene is extracted with light petroleum, an oil is dissolved, and from this, by treatment with alcoholic potash, a substance is obtained which crystallises from alcohol in yellowish needles, and melts at 140—146° ; it appears to be *tetrachloro-β-methylnaphthalene*, $C_{10}H_3MeCl_4$. It can also be obtained if the above-mentioned crude product is distilled under a pressure of 20 mm., as the fraction boiling at 220—227°. The yellow oil that comes over at 189° is *dichloro-β-methylnaphthalene*, $C_{10}H_5MeCl_2$.

Chlorine was also passed into α-methylnaphthalene, and the resulting viscid oil treated with alcoholic potash ; an oil was formed, from which finally small, yellowish needles of *trichlor-α-methylnaphthalene*, $C_{10}H_4MeCl_3$, were obtained ; they melt at 145—146°, and dissolve in all solvents except water. No other definite compound could be isolated.

When chlorine is passed into boiling β-methylnaphthalene, the already known β-naphthylmethyl chloride, $C_{10}H_7 \cdot CH_2Cl$, melting at 47°, is obtained; no other more highly chlorinated compounds appear to be formed.

When chlorine is passed into α-methylnaphthalene heated to 250°, and the product distilled in a vacuum, *α-naphthylmethyl chloride*, $C_{10}H_7 \cdot CH_2Cl$, is obtained as a yellow oil boiling at 167—169° under 25 mm. pressure, and dissolving in all solvents except water; when boiled at the ordinary pressure, it loses hydrochloric acid. α-Naphthylmethylene chloride, $C_{10}H_7 \cdot CHCl_2$, appears to be also formed, but cannot be separated by distillation in a vacuum, as it readily decomposes.

When bromine is added to α-methylnaphthalene in direct sunlight, the already known brom-α-methylnaphthalene, boiling at 178—179° under 30 mm. pressure, is formed. When β-methylnaphthalene is chlorinated in direct sunlight and the product distilled in a vacuum, *chloro-β-methylnaphthalene*, $C_{10}H_6MeCl$, is obtained as a colourless oil, boiling at 159—161° at 25 mm. pressure, and dissolving in all solvents except water; the *picrate*, $C_{10}H_6MeCl,C_6H_3N_3O_7$, crystallises from alcohol in yellow needles melting at 106—107°. By treating α-methylnaphthalene with chlorine in direct sunlight, and fractionating the product in a vacuum, *chlor-α-methylnaphthalene*, $C_{10}H_6MeCl$, is obtained; it boils at 167—169° under 30 mm. pressure. The *picrate*, $C_{10}H_6MeCl,C_6H_3N_3O_7$, forms orange-yellow needles melting at 101—102°.

When α-methylnaphthalene is dissolved in acetic acid and treated with strong nitric acid, *mononitro-α-methylnaphthalene* is formed. It is a yellow oil boiling at 194—195° at 27 mm. pressure, and easily soluble in alcohol, ether, and acetic acid. C. F. B.

Action of Hypochlorous Acid on β-Naphthaquinone. By E. Bamberger and M. Kitschelt (*Ber.*, **25**, 133—136).—*Dihydroxy-β-naphthaquinone* [$O_2 : (OH)_2 = 1 : 2 : 3 : 4$], is obtained by the action of hypochlorous acid on β-naphthaquinone. The reaction probably takes place through the formation of a chlorhydrin and a glycol, although these two intermediate compounds have not been detected. The dihydroxyquinone is isomeric with naphthazarin, and the author names it *isonaphthazarin*. It is extremely like naphthazarin in both physical and chemical properties. The following is the method of preparation:—Bleaching powder (35 grams) is suspended in water (135 grams), allowed to remain one hour, and then mixed with a solution of potassium carbonate (26 grams) in water (40 grams). After remaining two hours, the mixture is filtered, and boric acid (20 grams) added to the filtrate with shaking, and then allowed to remain one hour, filtered, and finely powdered β-naphthaquinone (2·5 grams) added to the filtrate with constant shaking. The pale-yellow solution is then mixed with concentrated hydrochloric acid and heated, until it suddenly changes to a dark red. On allowing the solution to remain, the isonaphthazarin crystallises out, mixed with boric acid, from which it is separated by boiling with water. The product is also mixed with a trace of a dye, soluble in alkali

with a red coloration, from which it is separated by crystallisation from acetone. It crystallises in beautiful, orange-red leaflets having a green lustre, sublimes in needles of metallic lustre, melts at 276°, is easily soluble in acetone, somewhat sparingly so in hot water, chloroform, and alcohol, and only very sparingly in cold water, ether, and benzene; it dissolves in concentrated sulphuric acid with a dark, cherry-red coloration; in fixed alkalis with a cornflower-blue, and in alkaline carbonates and ammonia with a violet-blue coloration. The alkaline solution is completely decolorised by long exposure to light. The sodium and copper salts are dark blue, the barium and zinc salts bright blue, the lead, cadmium, and nickel salts indigo-blue, the mercury and cobalt salts greenish-blue.

If the conditions of preparing the dye be only slightly varied, it is not formed at all, but a beautifully crystalline, colourless acid is obtained, melting at 203°. The authors are investigating the latter compound. E. C. R.

Action of Phosphorus Pentachloride on the Methyl Naphthyl Ketones. By J. A. Leroy (*Compt. rend.*, **113**, 1056—1059).—When methyl α-naphthyl ketone, boiling at 296—298°, is allowed to fall drop by drop on phosphorus pentachloride, hydrogen chloride is disengaged, and *chlor-α-naphthylethylene*, $C_{10}H_7{\cdot}CCl{:}CH_2$, remains as a colourless liquid which boils at 184° under a pressure of 50—60 mm., and has a sp. gr. of 1·179. It forms an additive compound with bromine. When methyl β-naphthyl ketone, melting at 51—52°, is substituted for its isomeride, the corresponding *chloro-β-naphthylethylene* is formed as a colourless solid which melts at 52—53°. Another chlorinated derivative is produced, however, at the same time, which crystallises in slender needles, melts with decomposition at about 165°, and is sparingly soluble in boiling water. By treating either of these ethylene derivatives with alcoholic potash, hydrogen chloride is eliminated, and the corresponding naphthylacetylene formed. An ethoxide, $C_{10}H_7{\cdot}C(OEt){:}CH_2$, is also produced by a second reaction, but its amount may be diminished by using very concentrated, dry, alcoholic potash, and not heating above 120°. The α-naphthylacetylene is purified by means of the silver compound, the copper compound not being adapted for this purpose on account of the readiness with which it is oxidised. The product of the alcoholic potash reaction is treated with alcoholic ammoniacal silver nitrate, and *silver-α-naphthylacetylene*, $C_{10}H_7{\cdot}C{:}CAg$, is precipitated as a yellowish-white powder, from which the hydrocarbon is set free by the addition of the theoretical quantity of hydrochloric acid.

α-Naphthylacetylene, $C_{10}H_7{\cdot}C{:}CH$, is a colourless liquid, which boils at 143—144° under a pressure of 25 mm., and has a sp. gr. of 1·057. It combines with bromine in carbon bisulphide solution to form liquid *dibrom-α-naphthyletkylene*, $C_{10}H_7{\cdot}CBr{:}CHBr$. This substance takes up more bromine in the dark, but no definite compound could be isolated from the product. The hydrocarbon is reconverted into the ketone by somewhat dilute (3 : 1) sulphuric acid. When the copper-α-naphthylacetylene is suspended in alcoholic ammonia and shaken with air, yellowish-white crystals of *dinaphthyldiacetylene*,

$C_{10}H_7 \cdot C{:}C \cdot C{:}C \cdot C_{10}H_7$, are deposited on the sides of the vessel. This substance melts at 171°, and is very soluble in benzene and carbon bisulphide, but less soluble in alcohol and acetic acid. It is more quickly obtained by oxidising the copper compound with alkaline potassium ferricyanide at a moderate temperature, but is then more difficult to purify. In carbon bisulphide solution, it absorbs an amount of bromine vapour corresponding with nearly eight equivalents, but a crystalline substance could not be isolated from the product. Dinaphthyldiacetylene combines with picric acid to form an additive compound, $C_{24}H_{14},C_6H_2(NO_2)_3 \cdot OH$, which crystallises in brilliant, red needles, and melts at 180°.

β-Naphthylacetylene, $C_{10}H_7 \cdot C{:}CH$, as obtained from chloro-β-naphthylethylene by treatment with alcoholic potash, forms colourless crystals, melts at 36°, and can be distilled under reduced pressure. It is soluble in alcohol, ether, and carbon bisulphide, and forms an additive compound with bromine, but this could not be crystallised. Ammoniacal silver nitrate precipitates *silver β-naphthylacetylene*, $C_{10}H_7 \cdot C{:}CAg$, as a white powder. Ammoniacal cuprous chloride throws down a canary-yellow precipitate. The hydrocarbon is reconverted into the ketone by somewhat dilute sulphuric acid.

Jn. W.

Julole. By A. Reissert (*Ber.*, **25**, 108—119; see also Abstr., 1891, 736).—This paper contains an account of the products of oxidation and reduction of α_1-keto-γ_1-methyljuloline.

$\alpha_1\alpha_2$-Diketo-γ_1-methyljulole, $C_{13}H_9NO_2$, is obtained, together with hydroxylepidinecarboxylic acid, by oxidising ketomethyljuloline with potassium permanganate. It is separated from the crystalline mixture thus obtained by extracting the hydroxylepidinecarboxylic acid with ammonia and crystallising the residue from dilute acetic acid. It crystallises in small, pale-yellow needles, is very electric, melts at 245° (corr.), is easily soluble in alcohol, acetic acid, and chloroform, less so in benzene, sparingly in boiling water, and insoluble in light petroleum. It dissolves in concentrated mineral acids, and is precipitated on the addition of water. When oxidised in acid solution with potassium permanganate, it is converted into hydroxylepidinecarboxylic acid. It does not yield a hydrazone when treated with phenylhydrazine. It is also obtained mixed with hydroxylepidinecarboxylic acid by using chromic acid as the oxidising agent. If potassium dichromate is added to a sulphuric acid solution of ketomethyljuloline, the *chromate* of the latter separates out in yellow needles. This salt is very unstable, cannot be recrystallised, and is easily decomposed by boiling with water or dilute acids.

Ketomethyljuloline is very stable towards acid reducing agents, and is not attacked when boiled for six hours with tin and hydrochloric acid or with zinc-dust and acetic acid. When distilled over zinc-dust, it yields resinous products, and part remains unaltered. It is, however, reduced by sodium amalgam in acetic acid solution, and also by sodium amalgam and alcohol, and by sodium and alcohol. With sodium amalgam and acetic acid, it yields bisketomethyljulolidyl and ketomethyljulolidine; with sodium amalgam and alcohol, it

yields a compound which the author believes to be α_1-hydroxy-γ_1-methyljuloline; and with sodium and alcohol, it yields γ-methyljulolidine.

α_1-Keto-γ_1-methyljulolidine is obtained by adding a large excess of 8 per cent. sodium amalgam to an acetic acid solution of ketomethyljuloline. From time to time more acetic acid is added, so as to keep the solution strongly acid. The solution is filtered and the product precipitated with alkali, the precipitate treated with dilute acetic acid, and the residue dissolved in acetic acid. On adding water to the solution, ketomethyljulolidine separates as a white, crystalline precipitate. It crystallises from dilute acetic acid in small, branching needles, melts at 242° (corr.), is very easily soluble in alcohol, ether, benzene, chloroform, and acetic acid, sparingly so in light petroleum, and insoluble in water.

Bis-α_1-keto-γ_1-methyljulolidyl, $C_{26}H_{28}N_2O_2$, is obtained by adding excess of alkali to the acetic acid mother liquors of the preceding compound. It crystallises from very dilute acetic acid in hard, lustrous crystals, melts at 257·5° (corr.), and has the same solubility as the preceding compound. A molecular weight determination gave the number 412, whilst the above formula requires 400.

α_1-Hydroxy-γ_1-methyljuloline is obtained by adding 8 per cent. sodium amalgam (150 grams) in 30-gram lots to a boiling solution of ketomethyljuloline (5 grams) in 98 per cent. alcohol (200 grams), and boiling the mixture until all the amalgam is destroyed. The mixture is allowed to cool, filtered, diluted with water, neutralised with hydrochloric acid, the alcohol distilled off, and the solution extracted with ether. The greater part of the ether is distilled off, and the remaining liquid dried with potassium carbonate. The dry product is then fractionally distilled, when a colourless oil is obtained boiling above 300°; it solidifies in a desiccator to a crystalline mass of greasy granules, and then melts at 45° (corr.). It is easily soluble in most solvents, always separates from its solutions as an oil, is dissolved by concentrated mineral acids, and precipitated on the addition of water; it is not soluble in alkalis. The presence of the hydroxyl group could not be detected; the compound is not attacked by acetic anhydride and sodium acetate, benzoic chloride or methyl iodide, and sodium.

α_1-Hydroxy-γ_1-methyl-$\beta_1\gamma_1$-dibromojulolidine, $C_{13}H_{15}NOBr_2$, is obtained by gradually adding bromine (1 mol.) dissolved in acetic acid to hydroxymethyljuloline dissolved in 10 times the quantity of acetic acid. The mixture, after a time, deposits small, yellow crystals of the new compound; this darkens on heating in a capillary tube, and melts about 141·5° with decomposition. The product contains the dibromide of monobromohydroxymethyljuloline, but as it cannot be recrystallised without decomposition, it was not obtained pure.

α_1-Hydroxy-β_1-bromo-γ_1-methyljuloline, $C_{13}H_{14}NOBr$, is obtained from hydroxymethyldibromojulolidine and from hydroxymethyltribromojulolidine by boiling them with water, when the former loses hydrogen bromide, the latter, bromine. The same decomposition takes place on boiling it with alcohol. It crystallises from dilute alcohol in small, white, lustrous crystals, melts at 80·5° (corr.), and is extremely

soluble in alcohol, ether, acetic acid, benzene, chloroform, and warm light petroleum, sparingly so in water.

α_1-*Hydroxy*-$\beta_1\beta_1\gamma_1$-*tribromo*-γ_1-*methyljulolidine*, $C_{13}H_{14}NOBr_3$, is obtained by allowing a mixture of the preceding compound (1 mol.) and bromine (1 mol.) dissolved in acetic acid to remain for some time. It crystallises in yellowish-red needles, melts about 140° with decomposition, gives off bromine when dried in a desiccator, and also when boiled with water, and is converted into bromhydroxymethyljuloline.

γ-*Methyljulolidine* is obtained on adding sodium (25 grams) to a boiling solution of ketomethyljuloline (10 grams) in absolute alcohol (250 grams). The mixture is allowed to cool, mixed with water, the alcohol distilled off, and the residue steam-distilled. A pale-yellow oil is obtained which is extracted with ether, the ether partly distilled off, and the remaining liquid dried with potassium carbonate and fractionally distilled. It boils at 283—287° with slight decomposition, has a characteristic, very unpleasant odour, and is very unstable. It is a strong base, and dissolves easily in mineral acids, but the salts are very unstable and were not obtained pure; the solutions of the salts give sparingly soluble and very unstable double salts with salts of the heavy metals. The free base is coloured blood-red by ferric chloride. The *picrate*, obtained on adding an alcoholic solution of picric acid to an alcoholic solution of the base, crystallises in broad, yellow spears, cannot be recrystallised without decomposition, darkens when dried at 100°, and blackens at 130—140°, when it decomposes and partially melts. E. C. R.

Dyes obtained from Ketomethyljuloline and Methyllepidone. By A. Reissert (*Ber.*, **25**, 119—123).—When ketomethyljuloline is treated with phosphorus pentachloride, 3 mols. of the ketone condense, and a violet dye of the formula $C_{39}H_{36}N_3O_3Cl$ is obtained. This loses hydrogen chloride when boiled with sodium hydroxide, and a dye of the formula $C_{39}H_{35}N_3O_3$ is obtained, which differs but slightly from the chlorinated compound. The author names these compounds "julole-violet" and "julole-violet base" respectively. Methyllepidone treated in the same way yields similar derivatives of the formulæ $C_{33}H_{29}N_3O_2Cl_2$ and $C_{33}H_{27}N_3O_2$.

Julole-violet is prepared by mixing ketomethyljuloline (4 grams) with phosphorus pentachloride (3 grams), adding sufficient phosphorus oxychloride to make the mixture damp, and heating it in an oil-bath at 150° until all action has ceased. The phosphorus oxychloride and trichloride are then distilled off, the product dissolved in concentrated hydrochloric acid, the brown solution filtered, diluted with water, and precipitated with sodium hydroxide. The precipitate is washed with a small quantity of water, then dissolved in hot water, and the solution filtered and evaporated to dryness. It is a violet substance having a strong metallic lustre, and is very easily soluble in water, from which it is precipitated on adding sodium hydroxide; it is soluble in alcohol, benzene, and acetic acid with a beautiful violet coloration, and in mineral acids with a brown coloration, but is only sparingly soluble in

light petroleum and ether. It has only one-tenth the dyeing power of the triphenylmethane dyes.

Julole-violet base is obtained by boiling julole-violet with sodium hydroxide. It is a dark-brown, amorphous mass, is only slightly soluble in water, giving a bright, reddish-violet solution easily soluble in alcohol, acetic acid, and mineral acids, and sparingly so in ether. The acetic acid solution imparts a dirty violet shade to textile fibres. The *platinochloride*, $C_{39}H_{35}N_3O_3,H_2PtCl_6$, is obtained as a dark-blue, amorphous powder on adding platinic chloride to a concentrated solution of the base in hydrochloric acid.

Lepidone-violet is obtained in a manner similar to julole-violet by heating equal weights of methyllepidone and phosphorus pentachloride. It has similar properties to julole-violet.

Lepidone-violet base is a dark-brown, amorphous powder, insoluble in water, and has similar properties to the julole compound. The *platinochloride* has the formula $C_{33}H_{27}N_3O_2,H_2PtCl_6$. E. C. R.

Derivatives of Carvole. By O. Wallach (*Ber.*, **24**, 3984—3991).—By reducing carvoxime with sodium amalgam, Goldschmidt obtained a base which he named carvylamine, and to which he assigned the composition $C_{10}H_{15}\cdot NH_2$ (Abstr., 1887, 475); the same compound was prepared by Leuckart and Bach (Abstr., 1887, 376) by distilling carvole with ammonium formate. According to Lampe (*Inaug. Dissert.*, Göttingen, 1889), carvylamine undergoes decomposition on distillation, yielding ammonia and cymene.

The author finds that *dihydrocarvylamine*, $C_{10}H_{17}\cdot NH_2$, is produced when carvole is heated with ammonium formate, the base obtained from dextrocarvole being dextrorotatory, that produced from lævocarvole, lævorotatory; it boils at 94—95° under a pressure of 16 mm., absorbs carbonic anhydride from the air, and has a sp. gr. of 0·889 at 20°. The hydrochloride is precipitated when hydrogen chloride is passed into an ethereal solution of the dextrorotatory base; this salt melts at about 183—184°, and decomposes when heated, yielding an oil and ammonium chloride, without formation of any bye-products. The oil obtained in this way is readily oxidised by potassium permanganate in the cold, and combines directly with bromine; it is optically active, and its sp. gr. is 0·847 at 20°. It consists of a mixture of terpinene and cymene which cannot be separated by fractional distillation; the first-named compound was identified by means of its nitrosite (m. p. 155°). The cymene remains unchanged on treating the oil with potassium permanganate in the cold, whereas the terpinene undergoes oxidation; after distilling with steam, the cymene was oxidised with boiling potassium permanganate solution, its presence being proved by the formation of terephthalic acid and parahydroxyisopropylbenzoic acid. Unless other compounds are present in the original oil, it follows that terpinene can exist in an optically active modification, which is rendered inactive by treatment with acids, and also on conversion into the nitrosite; assuming the correctness of Goldschmidt's formula for carvole, these results lead to the conclusion that terpinene is a true hydrocymene.

Dihydrocarveol, $C_{10}H_{17}\cdot OH$, is obtained when dihydrocarvylamine is

treated with nitrous acid; it boils at 224°, has a sp. gr. of 0·935 at 22°, and its refractive power is $[n]_D = 1·48506$. Dihydrocarveol is also obtained when carvole is reduced with sodium and alcohol; this substance boils at 224—225°, has a sp. gr. of 0·927 at 20°, and its refractive power is $[n]_D = 1·48168$. Whether these two compounds are identical or not has not yet been decided. When dihydrocarveol is boiled with dilute sulphuric acid, it is readily converted into an oil from which large quantities of terpinene nitrosite are obtained on treatment with nitrous acid; the oil seems also to contain cymene.

F. S. K.

Menthylamine. By O. Wallach (*Ber.*, **24**, 3992—3993).—*Menthylamine*, $C_{10}H_{19}·NH_2$, is formed when menthone is heated at 190—200° for some hours with ammonium formate, and the product decomposed with alcoholic potash. It is a colourless oil, of sp. gr. 0·862 at 20°, boils at 208—209°, and rapidly absorbs carbonic anhydride from the air; its refractive power is $[n]_D = 1·46058$. The *nitrate* and the *sulphate* are very readily soluble, but the *oxalate* and the *platinochloride* are only sparingly soluble in water; the *hydrochloride* crystallises well, is stable in the air, and, like the corresponding salts of other saturated bases (bornylamine, fenchylamine), sublimes with only very slight decomposition. The base combines readily with carbon bisulphide and with aldehydes; its *acetyl* derivative, $C_{10}H_{19}·NHAc$, is crystalline.

F. S. K.

Ethyl Camphorates and Isocamphorates. By C. Friedel (*Compt. rend.*, **113**, 825—832).—The author considers that in the camphoric acids there is only one carboxyl group, the second acid function arising from a hydroxyl group attached to a carbon atom which is connected with the carboxyl group, with the CO group of the original camphor, and with a CH_2 group. The carboxyl group is formed by the oxidation of the methyl group in Kekulé's formula, and the COH, CO, and CH_2 groups occupy the positions 1 : 2 : 6 respectively. the corresponding groups in the original camphor being C, CO, and CH. The proximity of the CO group confers on the OH group an acidic function comparable with that of the OH in a carboxyl group. The author shows that this view of the constitution of the camphoric acids makes it possible to explain the existence of dextro- and lævo-gyrate camphoric and isocamphoric acids, in accordance with the Le Bel-Van't Hoff hypothesis. This view is also supported by the formation of camphosulphonic acids in which the COOH group is replaced by HSO_4, a behaviour analogous to that shown by alcohol acids in which the hydroxyl group is attached to the same atom of carbon as the carboxyl group.

Camphoric acid behaves with phenolphthaleïn and methyl-orange in the same way as lactic acid, glycollic acid, &c. Berthelot has shown that the heat of neutralisation of the first acid function by sodium hydroxide is +13·57 Cal., and that of the second 12·9 Cal. The difference between the two acid functions is also shown by the properties of the ethyl salts.

Diethyl camphorate, obtained by the action of ethyl iodide on silver camphorate in presence of alcohol, is an oil boiling at 155° under a

pressure of 12—14 m.m.; sp. gr. at 0° = 1·0495; rotatory power $[\alpha]_D = +37° 42'$. When boiled with alcoholic potash, it yields a *monethyl camphorate*, a very viscous liquid which boils at 207—208° under a pressure of 22 mm. This monethyl camphorate dissolves in alkalis, and is precipitated by acids, whereas the diethyl salt is insoluble in alkalis; its sp. gr. at 0° is 1·1004, and its rotatory power $[\alpha]_D = +23° 54'$

Monethyl camphorate, obtained by the action of hydrogen chloride on an alcoholic solution of camphoric acid, boils at 216—219° under a pressure of 30 mm.; sp. gr. at 0° = 1·1133; rotatory power $[\alpha]_D = +39° 11'$. It is monobasic when phenolphthaleïn is used as the indicator. With aqueous potash, this compound yields alcohol and potassium camphorate, whereas the first monethyl salt, obtained from diethyl camphorate, is not saponified.

Diethyl isocamphorate, prepared from silver camphorate, boils at 165° under a pressure of 25—28 mm.; sp. gr. at 0° = 1·0473; rotatory power $[\alpha]_D = -48° 32'$. When boiled with alcoholic potash, it yields a *monethyl isocamphorate* which is very difficult to purify; it is a very viscous liquid soluble in alkalis. The *monethyl isocamphorate*, obtained by direct etherification, boils at 195—197° under a pressure of 18—20 mm., and is at first a very viscous liquid; sp. gr. at 0° = 1·1156; rotatory power $[\alpha]_D = -49° 31'$. After some time, however, it crystallises, and from alcohol it separates in rectangular octahedra melting at 75°. The fundamental form of the crystals is a rhombic prism of 96° 13′; $b : h = 0·8375 : 1$ and $d : D : h = 0·8971 : 1 : 1·6040$. This ethereal salt, when treated with aqueous potash, is easily saponified, and in this respect differs from the monethyl salt obtained from diethyl isocamphorate. C. H. B.

Digitonin. By H. Kiliani (*Ber.*, **24**, 3951—3954).—In a recent paper (this vol., p. 222), Houdas states that the portion of the digitalis glucosides which is soluble in water, and was termed by Nativelle digitaleïn, consists almost entirely of a single substance, namely, that described by Schmiedeberg and Kiliani as digitonin. The author states that this is not the case, although the alcoholic solution may, as stated by Houdas, be fractionally precipitated by ether without any separation taking place; by suitable means, it may be shown that Schmiedeberg's digitaleïn is really a mixture of 7 or 8 substances, and contains at most 60 per cent. of digitonin.

Houdas also states, without giving any analyses, that the addition of a fatty alcohol to a solution of digitaleïn, causes the precipitation of a crystalline compound containing alcohol of crystallisation. The author finds that this is quite incorrect so far as ethyl alcohol is concerned. Digitonin, after crystallisation from 85 per cent. alcohol, contains 5 mols. H_2O, which are evolved at 110°, leaving a substance of the composition $C_{27}H_{46}O_{14}$; it does not lose more water without undergoing simultaneous decomposition, whence it appears that the formula of digitonin is $C_{27}H_{46}O_{14}$, and not $C_{27}H_{44}O_{13} + H_2O$, as previously stated. The author also replies to the criticisms of Houdas on his formula for digitonin, and maintains the accuracy of his results.

The drug usually sold as "digitalin crist." consists almost entirely of digitonin, which is quite useless for medicinal purposes. Crystallised digitonin does not give a clear solution with 600 parts of cold water, and forms an opalescent solution with 50 parts of warm water; the solutions show the frothing observed by Nativelle and Schmiedeberg even in a dilution of 1 : 2000. H. G. C.

Linamarin. By A. Jorissen and E. Hairs (*Chem. Centr.*, 1891, ii, 702; from *Pharm. Post*, **24**, 659—660).—The authors have found hydrogen cyanide in the distillates from *Arum maculata*, *Ribes aur.*, *Aquilegia vulg.*, *Poa aquatic.*, and especially in the plumules of *Linum usitatissimum*. A glucoside was separated, named by them *linamarin*, which differs essentially from both amygdalin and laurocerasin. Linamarin forms groups of colourless needles having a cool and bitter taste. The analysis gave the following figures:—C = 47·88, H = 6·68, N = 5·55, O = 39·89. Both dilute mineral acids, as also an emulsion of linseed meal, liberate hydrogen cyanide from it. It is very readily soluble in cold water; it does not lose water at 100°, and is not decomposed at 150°; it melts at 34°. It is not coloured by concentrated sulphuric acid; an emulsion of sweet almonds is without influence on it. When it is decomposed, no benzaldehyde is formed. J. W. L.

Oxidation of Brasilin; New Derivative of Resorcinol. By C. Schall and C. Dralle (*Ber.*, **25**, 18—27; see also Abstr., 1888, 295; 1889, 55, 1004; 1890, 996).—Brasileïn, described by the authors in their last communication, readily unites with aluminium, chromium, and zinc to form crystalline lakes; these are best obtained by passing a current of air through an aqueous alkaline solution of brasilin, containing, in addition, a salt of the metal whose lake is required. An iron lake may be obtained in a similar manner, but the presence of alkali is, in this case, unnecessary. The lakes are soluble in alkalis and acids, but insoluble in indifferent solvents.

The tendency of brasilin to yield derivatives of brasileïn is still more prominent in the brominated derivatives; thus, if in the preparation of tribromobrasilin, acetic acid containing more than 10 per cent. of water is used, large quantities of tribromobrasileïn are formed.

The product obtained by the further oxidation of brasileïn, to which the authors ascribed the formula $C_9H_6O_4$ (Abstr., 1889, 55), is soluble in alkalis, and, therefore, probably contains one or more hydroxyl groups; this view has been confirmed by the preparation of the *methyl* and *acetyl* derivatives. The former is obtained by acting on the alcoholic solution of the oxidation product with sodium, subsequently adding methyl iodide, and heating at 100°. After evaporating off the alcohol and methyl iodide, the residue is extracted with ether, unaltered phenols removed by shaking the ethereal solution with dilute soda, the ether distilled off, and the residue recrystallised from alcohol. It separates in yellow scales, which become white on boiling with nitric acid, and melt at 169—170°. The analysis and molecular weight, as found by Raoult's method, and from the vapour

density under diminished pressure, show that its formula is $C_{11}H_{10}O_4$, or $C_9H_4O_2(OMe)_2$. The acetyl derivative, $C_9H_4O_2(OAc)_2$, is obtained by boiling the oxidation product with acetic anhydride and anhydrous sodium acetate, and crystallises from 50 per cent. acetic acid in long, slender, white needles, melts at 148—149°, is insoluble in cold, slightly soluble in hot water, and more readily in warm acetic acid.

The oxidation product gives precipitates with neutral solutions of the salts of many heavy metals, which may, with care, be obtained crystalline. The lead precipitate dissolves in hot, dilute acetic acid, and if soda be added until turbidity commences, the compound $(C_9H_6O_4)_2PbO + H_2O$ separates out in stellate tufts of needles. The phenol also gives substitution products with bromine, of the composition $C_9H_4Br_2O_4$ and $C_9H_3Br_3O_4$. The former crystallises in flesh-coloured, spear-shaped needles melting at 235°, and the latter in transparent, brownish prisms melting at 257—258°.

The above-mentioned dimethyl derivative yields, on oxidation with potassium permanganate and acetic acid, the paramethoxysalicylic acid described by Tiemann and Parisius (Abstr., 1881, 270). The formula of the oxidation product may, therefore, be resolved into $C_6H_3(OH)_2{\cdot}C_3HO_2$ [OH : OH : C_3HO_2 = 1 : 3 : 4]. So far as the group C_3HO_2 is concerned, no very definite conclusions can yet be drawn; the oxygen is not present as hydroxyl or carbonyl, and the authors suggest that it may possibly be a dioxytrimethylene group,  . In favour of the view that the oxygen atoms are combined in some such manner, is the observation that in the preparation of the dibromo-derivative a substance is also formed which appears to be an additive compound, $C_9H_6O_4(HBr)_2$; it crystallises in brownish-white needles, and becomes dark-brown at 210°. H. G. C.

Preparation of Flavin. By V. H. Soxhlet (*Chem. Zeit.*, **14**, 1345—1346).—The natural dye flavin is obtained from the bark of the oak by the following method:—The pulverised bark is digested under a pressure of 1—1½ atmospheres with dilute alkali, the extract is then separated from the residual bark by filtration, best with filter presses, the alkali nearly neutralised by the addition of acids or acid salts, and the precipitated flavin collected, dried, and ground. The extractors used are usually of copper, and are arranged in series of five or six, so connected together that the extract can circulate through the series. About 1000 kilos. of bark and 2000—2500 litres of water, with 50—70 grams of soda crystals, is the charge for each extractor. The contents of each extractor is brought to the boil five or six times, for one hour each, and the extract then has a density of 15—17° Be. (1·116—1·135 sp. gr.). Borax or ammonia liquor of 20° Be. (1·161 sp. gr.) are also employed instead of soda. After separating the exhausted bark, the extract is diluted with water, and again boiled with alkali, after which the latter is neutralised. Different acids are used, but a mixture of 2 parts of sulphuric acid and 3 parts of hydrochloric acid is very common. The alkali is nearly neutralised,

and the liquid heated to boiling; it is then filtered rapidly from the precipitated flavin, and the latter dried at a gentle heat and packed in boxes. From 4 to 10 per cent. of the dye is obtained.

J. W. L

Hydroxyxanthones. By S. v. Kostanecki and B. Nessler (*Ber.*, **24**, 3980—3984; compare Abstr., 1891, 1060).—When β-hydroxymethylxanthone is boiled with acetic anhydride and sodium acetate, it is converted into a crystalline *acetyl* derivative,

$$C_{13}H_6O_2Me\cdot OAc,$$

which melts at 127°.

β-Hydroxyxanthone, $C_{13}H_7O_2\cdot OH$, crystallises in colourless needles, melts at 242°, and dissolves in soda with a very slight yellow coloration.

Isoeuxanthone (m. p. 247°) is readily soluble in ammonia; its alcoholic solution gives a brown coloration with ferric chloride. When treated with sodium amalgam, it gives a faintly blood-red solution, which loses its colour after some time, and then yields a red precipitate on acidifying. *Diacetylisoeuxanthone*, $C_{13}H_6O_2(OAc)_2$, crystallises in colourless needles, and melts at 144°.

Hydroxydixanthone, $C_{20}H_{10}O_5$, is obtained, together with smaller quantities of another condensation product, in the preparation of isoeuxanthone by the method already described; it crystallises from glacial acetic acid in yellow plates, melts at 258°, and is only very sparingly soluble in alcohol; it forms an intensely yellow, almost insoluble sodium derivative, and a colourless acetyl derivative. The second condensation product crystallises from glacial acetic acid in yellow plates, does not melt below 320°, and dissolves in concentrated sulphuric acid with a green fluorescence, but is insoluble in soda; it is possibly a trixanthone.

Euxanthone is formed when quinolcarboxylic acid is distilled with resorcinol, but it is not produced from β-resorcylic acid and quinol under like conditions; in view of these facts, it is possible that euxanthone has the constitution represented by the formula

$$^{4}OH\cdot C_6H_3\langle{}^{1}_{CO}{>}O\rangle C_6H_3\cdot{}^{5}OH.$$

When salicylic acid is distilled with quinol, a small quantity of a yellow, crystalline compound is obtained; this substance melts above 320°, dissolves in soda with a yellow coloration, and is probably a hydroxyxanthone of the constitution $^{4}OH\cdot C_6H_3\langle{}^{1}_{CO}{>}O\rangle C_6H_4$.

F. S. K.

Base Obtained from Pyridine. By F. v. Hemmelmayr (*Monatsh.*, **12**, 533—540; compare Abstr., 1891, 1339). When the so-called chloromethyl alcohol of Lösekann (*Chem. Zeit.*, **14**, 1408—1409) is added, drop by drop, to an equal weight of well-cooled pyridine, a reddish-brown oil separates, which, if allowed to remain in the cold, gradually solidifies. The product cannot be purified, owing to its hygroscopic properties and the readiness with which it is resolved into its generators; but it gives well-characterised compounds with various

salts and acids. With mercuric chloride and platinic chloride, it forms respectively the compounds $OH{\cdot}CH_2{\cdot}C_5NH_5Cl,HgCl_2$, which crystallises from hot water in pale-red scales melting at 162°, and $(C_5NH_5,CH_2{\cdot}OH)_2PtCl_6$, which crystallises in beautiful, yellow prisms melting at 216°. With picric acid, the compound

$$OH{\cdot}CH_2{\cdot}C_5NH_5{\cdot}O{\cdot}C_6H_2(NO_2)_3$$

is obtained. It crystallises from hot water in long, yellow prisms, and melts at 200°. The compound with sulphuric acid has not been isolated in the crystalline form, but the compound with nitric acid, $OH{\cdot}CH_2{\cdot}C_5NH_5{\cdot}NO_3$, is obtained in the form of colourless prisms, when its alcoholic solution, prepared by treating the original substance with silver nitrate, is mixed with ether.

The analysis of its compounds leaves no doubt that the condensation product has the formula $C_5NH_5,CH_2Cl{\cdot}OH$, in which the radicles $CH_2{\cdot}OH$ and Cl are probably separately attached to the nitrogen of the pyridine. When heated with potash, or when distilled, the product is resolved into formaldehyde and pyridine; the latter seems also to be one of the products of oxidation by permanganate. Attempts to displace the chlorine by hydroxyl by the use of silver oxide, give rise to the formation of metallic silver and pyridine.

Quinoline also unites with chloromethyl alcohol, but the product has not yet been obtained in quantity sufficient to determine its properties. G. T. M.

Synthesis of β-Chloroquinaldine. By A. Busch and W. Koenigs (*Ber.*, **24**, 3962—3963).—By the action of butylchloral on aniline in presence of zinc chloride and hydrochloric acid, the authors hoped to obtain γ-methylquinoline or lepidine; instead of this they obtained the β-chloroquinaldine described by Magnanini (Abstr., 1887, 1113), the reaction taking place as follows :—

$$C_6H_4{<}\begin{matrix}H\\NH_2\end{matrix} + \begin{matrix}COH{\cdot}CHCl\\Cl_2CMe\end{matrix} = C_6H_4{<}\begin{matrix}CH{:}CCl\\N{=}CMe\end{matrix} + H_2O + 2HCl.$$

The mixture of butylchloral, aniline hydrochloride, zinc chloride, and hydrochloric acid is heated for eight hours at 160—180°, the product dissolved in hot, dilute sulphuric acid, filtered from resinous matters, and freed from unaltered butylchloral by extraction with ether. The aniline present is converted into phenol by the action of sodium nitrite, and the filtered solution made alkaline, and extracted with ether; the base is then extracted from the ethereal solution by dilute sulphuric acid, the acid solution again made alkaline, and taken up with ether, the latter evaporated, and the residue distilled in a current of steam. The base then passes over in oily drops, which quickly solidify, and on recrystallisation from alcohol forms slender, colourless needles melting at 71—72°. Its *picrate* forms pale-yellow, sparingly soluble needles, and melts at 220—224° with decomposition. The other properties of β-chloroquinaldine were found to be in full agreement with the description given by Magnanini. H. G. C.

Constitution of Orthohydroxyazo-Dyes. By S. Ganelin and S. v. Kostanecki (*Ber.*, **24**, 3976—3980).—The investigations of Noelting and Trautmann (Abstr., 1891, 325) and of Kostanecki (Abstr., 1891, 579) have shown that derivatives of orthohydroxyquinoline [N : OH = 1′ : 1] have the property of dyeing mordanted cotton only as long as the hydroxyl group in the 1-position remains unchanged; Matheus' phenylazorthohydroxyquinoline (Abstr., 1888, 851), as was to be expected, obeys this rule.

Metaphenylazorthohydroxymethylquinoline,

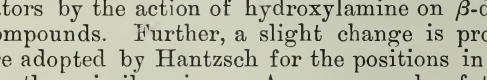
$$C_9NH_4Me(OH)\cdot N_2Ph\ [Me : OH : N_2Ph = 4 : 1 : 2],$$

can be prepared by treating a hydrochloric acid solution of orthohydroxymethylquinoline with a solution of diazobenzene chloride and then pouring the mixture into dilute alkali. It crystallises from acetic acid in carmine-red needles, melts at 120°, and is only very sparingly soluble in boiling water and hot alkalis, but soluble in concentrated sulphuric acid with a yellowish-red coloration. The fact that this compound has the property of dyeing mordanted cotton is strong evidence that it is an azo-compound and not a hydrazone.

Metamidorthohydroxymethylquinoline, $C_9NH_4Me(OH)\cdot NH_2$, is obtained when the preceding compound is treated with tin and hydrochloric acid: it is also formed when the metanitrosoorthohydroxymethylquinoline described by Noelting and Trautmann is treated in like manner. It separates from benzene, in which it is very readily soluble, in large, broad crystals melting at 139°. The *hydrochloride*, $C_{10}N_2H_{10}O,HCl$, crystallises from hot water in long, red prisms.

F. S. K.

Isoxazoles. By L. Claisen (*Ber.*, **25**, 3900—3918).—This paper contains a general sketch of the various classes of isoxazoles, isoxazolecarboxylic acids, and di-isoxazoles, prepared by the author and his collaborators by the action of hydroxylamine on β-diketones and analogous compounds. Further, a slight change is proposed in the nomenclature adopted by Hantzsch for the positions in the isoxazole ring and in other similar rings. As an example of the formation of an isoxazole, the action of hydroxylamine on acetylacetone, $COMe\cdot CH_2\cdot COMe$, may be taken; a monoxime is, presumably, first formed, but this cannot be isolated; it immediately loses water, forming $\alpha\gamma$-dimethylisoxazole:—



Acetylacetone monoxime. $\alpha\gamma$-Dimethylisoxazole.

The ketone is dissolved in acetic acid and heated with hydroxylamine hydrochloride for 1—2 hours on the water-bath until it no longer gives a red colour with ferric chloride; the product is then diluted with water, made alkaline with soda, and the isoxazole extracted with ether. The yield varies from 50 to 80 per cent. of the ketone used.

Dunstan and Dymond (Trans., 1891, 410) have shown that when the trimethylisoxazole obtained by the action of alkalis on nitroethane

is reduced with sodium, it yields a compound $C_6H_{11}NO$. They assume that this compound has a ring structure, and, on this assumption, base an argument that the β-diketones are ring compounds. This view is controverted by the author, who, by the reduction of $\alpha\gamma$-dimethylisoxazole with sodium, obtained a substance identical with that formed when ammonia acts on acetylacetone. He also, in a similar manner, obtained Dunstan and Dymond's compound by acting on methylacetylacetone, COMe·CHMe·COMe, with ammonia; this compound has then the constitution COMe·CHMe·CMe:NH or COMe·CMe:CMe·NH_2, and is not a ring compound. Consequently there is no reason to suppose that a β-diketone has a ring structure either. C. F. B.

Dimethyldiazine. By C. Stoehr (*Ber.*, **24**, 4105—4110; compare Abstr., 1891, 581).—Dimethyldiazine, $C_4N_2H_2Me_2$, has been previously described; it boils at 153—153·5° under a pressure of 752·5 mm. The *hydrochloride*, $C_6H_8N_2$,HCl, crystallises from absolute alcohol in colourless needles, and is very readily soluble in water. The *picrate* is deposited from water in flat, lustrous needles melting at 142—143°. The *nitrate*, *sulphate*, and *chromate* readily dissolve in water. *Dimethyldiazine methiodide*, $C_6H_8N_2$,MeI, is formed at ordinary temperatures from dimethyldiazine and methyl iodide, and crystallises from absolute alcohol in pale-yellow prisms which melt at 230°; it yields a *periodide* crystallising in reddish-brown needles, and also a colourless, crystalline double salt with cadmium iodide. The corresponding *methochloride* is very soluble in water, and yields crystalline salts with platinic chloride, auric chloride, and mercuric chloride.

Dimethyldiazine combines with anhydrous bromine with evolution of heat; the product is crystalline and decomposes at 170°; in aqueous solution, a second additive compound is formed, which crystallises in long needles and undergoes dissociation at ordinary temperatures.

Diazinedicarboxylic acid, $C_4N_2H_2(COOH)_2 + 2H_2O$, is prepared by the oxidation of the base with potassium permanganate, and melts at 255—256°, not at 250° as previously stated; it is soluble in dilute mineral acids, and resembles the α-pyridinecarboxylic acids in its colour reactions. The *ammonium salt* crystallises from alcohol in needles; the *silver salt* is amorphous; the *barium salt* is deposited in colourless, lustrous plates; the *calcium* and *lead salts* are also crystalline.

Hexahydrodimethyldiazine, $C_6N_2H_{14}$, is obtained by the reduction of the diazine with sodium in alcoholic solution; it is volatile with steam and miscible with water in all proportions, but is precipitated as a colourless oil on the addition of potash; it combines with sodium and potassium hydroxides and also with barium dioxide, and is insoluble in ether. The *hydrochloride*, $C_6N_2H_{14}$,2HCl, is deposited from water in large, lustrous crystals, and from alcohol in colourless needles which decompose above 300°. The *platinochloride*, $C_6N_2H_{14}$,$H_2PtCl_6 + 3H_2O$, crystallises in long prisms; the *aurochloride* is crystalline; and the *mercurochloride* readily soluble in water. The *picrate* is deposited in small, lustrous, yellow needles which decompose without melting. The *dinitrosamine*, $C_6N_2H_{12}(NO)_2$, is obtained by the action

of sodium nitrite on the hydrochloride, and crystallises from alcohol in long, colourless, lustrous, prismatic needles melting at 170—171° the compound gives a blue colour with phenol and sulphuric acid.

J. B. T.

Biazolones. By M. Freund and others (*Ber.*, **24**, 4178—4204; compare Freund and Kuh, Abstr., 1890, 1440).—*β-Naphthylmethylbiazolone*, $C_{10}H_7\cdot N<\begin{matrix}N=CMe\\ |\\ CO\cdot O\end{matrix}$, is obtained by heating acetylnaphthylhydrazine (m. p. 167°) with an excess of carbonyl chloride dissolved in toluene, in a sealed tube at 100° for 2—3 hours, and, after evaporating the solvent, crystallising the product several times from dilute alcohol; it forms white, silky needles, melts at 125°, and is readily soluble in alcohol, ether, benzene, and chloroform, but almost insoluble in water.

β-Naphthylmethyl-ψ-thiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=CMe\\ |\\ CS\cdot O\end{matrix}$, is prepared by boiling acetylnaphthylhydrazine with an excess of thiocarbonyl chloride dissolved in benzene in a reflux apparatus, and, after allowing the solvent to evaporate, repeatedly crystallising from alcohol with the addition of animal charcoal; it crystallises in small, faintly yellow, lustrous needles, melts at 109°, and is somewhat sparingly soluble in boiling water.

Phenyl-β-naphthylthiosemicarbazide, $C_{10}H_7\cdot N_2H_2\cdot CS\cdot NHPh$, obtained by mixing molecular proportions of naphthylphenylhydrazine and phenylthiocarbimide dissolved in alcohol, crystallises from alcohol in white leaflets, melts at 202°, and is readily soluble in alcohol and chloroform, sparingly in benzene and ether, and insoluble in water.

β-Naphthylanilidothiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=C\cdot NHPh\\ |\\ CO\cdot S\end{matrix}$, is produced by allowing finely-powdered phenyl-β-naphthylthiosemicarbazide to remain in a closed flask with an excess of carbonyl chloride dissolved in toluene at the ordinary temperature for 24 hours, shaking at intervals; the solvent is allowed to evaporate, the residue extracted with alcohol to remove the unaltered carbazide, and crystallised from benzene; it forms white, flocculent crystals, melts at 198—199°, and is almost insoluble in water, sparingly soluble in alcohol and ether, but readily so in benzene and chloroform.

β-Naphthylamidobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=C\cdot NH_2\\ |\\ CO\cdot O\end{matrix}$, prepared in the same manner as the last-mentioned compound from β-naphthylsemicarbazide and carbonyl chloride, crystallises from alcohol in small, almost white, prismatic needles, melts at 227°, is sparingly soluble in ether and benzene, and insoluble in water and chloroform.

β-Napthylamidothiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=C\cdot NH_2\\ |\\ CO\cdot S\end{matrix}$, is obtained in the form of yellowish leaflets by shaking β-napthylthiosemicarbazide with a solution of carbonyl chloride, allowing the solvent to evaporate, and repeatedly crystallising from alcohol; it melts at 220°,

and is readily soluble in alcohol, chloroform, and benzene, but insoluble in water and ether.

Oxalyl-β-naphthylhydrazine, $C_2O_2(N_2H_2\cdot C_{10}H_7)_2$ (?), is formed when β-naphthylhydrazine and ethyl oxalate are boiled together in molecular proportion; after adding absolute alcohol and allowing the product to cool, reddish-brown crystals separate, which are dried on a porous plate and extracted with absolute alcohol, when the compound, which is insoluble in ordinary solvents and melts at 277°, remains; whilst *ethyl oxalate β-naphthylhydrazide*, $C_{10}H_7\cdot N_2H_2\cdot CO\cdot COOEt$, separates on allowing the alcoholic filtrate to remain; this melts at 159°, and is almost insoluble in water. When the last-mentioned compound is dissolved in alcohol, and alcoholic potash added, the potassium salt of the corresponding acid separates, and the *acid* is precipitated on adding concentrated hydrochloric acid to its solution in a little water; it forms small, white needles, melts at 202°, and is readily soluble in glacial acetic acid, very sparingly in benzene, chloroform, and ether, and insoluble in water.

Acetyl-α-naphthylhydrazine, $C_{10}H_7\cdot N_2H_2Ac$, prepared by mixing the dried base (m. p. 115—116°) with an excess of acetic anhydride, crystallises from dilute alcohol in colourless needles, melts at 143°, and is sparingly soluble in hot water.

α-Naphthylmethylbiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=CMe\\ CO\cdot O\end{matrix}$, is obtained by heating the last-mentioned compound with an excess of carbonyl chloride dissolved in toluene in a sealed tube at 100° for about two hours; it crystallises from alcohol in colourless needles, melts at 89°, and is insoluble in water.

α-Naphthylmethyl-ψ-thiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=CMe\\ CS\cdot O\end{matrix}$, is produced by dissolving acetyl-α-naphthylhydrazine in chloroform (10 parts) and boiling it for an hour with the gradual addition of a slight excess of thiocarbonyl chloride; the solvent is allowed to evaporate, the residue repeatedly redissolved in chloroform, and precipitated with light petroleum, and finally crystallised from dilute alcohol, when it separates in bright-yellow needles, melts at 86°, and is readily soluble in alcohol and benzene, sparingly in ether, and insoluble in light petroleum and water.

Benzoyl-α-naphthylhydrazine, $C_{10}H_7\cdot N_2H_2Bz$, separates as a yellowish precipitate on adding the calculated quantity of benzoic chloride to a cooled solution of α-naphthylhydrazine dissolved in ether (10 parts); after washing with water, it is crystallised from dilute alcohol, and forms needles, melts at 184°, and is readily soluble in alcohol, ether, and benzene, but insoluble in water and light petroleum.

α-Naphthylphenylbiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$, is prepared by heating the last-described benzoyl derivative with an excess of carbonyl chloride dissolved in toluene in a sealed tube at 100° for an hour, decanting the clear, brown solution from the accompanying resin, allowing it to evaporate, and crystallising the residue first from benzene and afterwards from alcohol; it forms colourless, felted

needles, melts at 136°, is readily soluble in ether and light petroleum, but insoluble in water, and is not decomposed by boiling with sodium hydroxide solution.

α-Naphthylphenyl-ψ-thiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=CPh\\ CS\cdot O\end{matrix}$, is obtained by gradually adding the calculated quantity of thiocarbonyl chloride to benzoyl-α-naphthylhydrazine dissolved in chloroform (10 parts), heating in a reflux apparatus until the evolution of hydrogen chloride ceases, allowing the solution to evaporate, redissolving the residue in chloroform, shaking with light petroleum to precipitate the resinous substances, again evaporating, and crystallising from dilute alcohol, when it separates in colourless needles, melts at 164°, and is insoluble in water.

α-Naphthylthiocarbizine, $C_{10}H_7\cdot N<\begin{matrix}CS\\ NH\end{matrix}$, is prepared by heating α-naphthylthiosemicarbazide (see below) (10 grams) with 20 per cent. hydrochloric acid (30 c.c.) in a sealed tube at 130° for 12 hours, washing the crude melt with water, boiling it with water and animal charcoal, and adding concentrated hydrochloric acid to the filtrate, whereby the hydrochloride is precipitated in white needles melting at 230°; it yields the free base when treated with sodium carbonate solution; the latter crystallises from alcohol in colourless needles, melts at 184—185°, does not reduce Fehling's solution, gives a violet colour with bleaching powder and sulphuric acid, and is almost insoluble in water. The *acetyl* derivative, $C_{10}H_7\cdot N<\begin{matrix}CS\\ NAc\end{matrix}$, crystallises from alcohol in long, colourless needles, and melts at 283°; the *benzoyl* derivative separates from benzene in almost colourless crystals, and melts at 175—176°.

α-Naphthylamidobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=C\cdot NH_2\\ CO\cdot O\end{matrix}$, is produced by allowing α-naphthylsemicarbazide (Pinner, *Ber.*, **20**, 2358) to remain with an excess of carbonyl chloride dissolved in toluene in a closed vessel for 24 hours with frequent shaking; it crystallises from alcohol in colourless leaflets which become brown in the air, melts at 212°, and is insoluble in water.

α-Naphthylamido-ψ-thiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N=C\cdot NH_2\\ CS\cdot O\end{matrix}$, is obtained by heating α-naphthylsemicarbazide with thiocarbonyl chloride in molecular proportion together with benzene in a closed vessel at 80° for half an hour, and then keeping the mixture at a moderate temperature for 12 hours; it crystallises from alcohol in microscopic, yellowish needles, melts at 218°, and is insoluble in water, ether, and carbon bisulphide.

α-Naphthylthiosemicarbazide, $C_{10}H_7\cdot N_2H_2\cdot CS\cdot NH_2$, is prepared by boiling ammonium thiocyanate and α-naphthylhydrazine hydrochloride (equal weights) with $2\frac{1}{2}$ times the weight of absolute alcohol for 15 hours, collecting, washing with water, and crystallising from

alcohol, when it separates in colourless, hexagonal tablets, melts at 209°, and is insoluble in ether, chloroform, and water.

α-Naphthylamidothiobiazolone, $C_{10}H_7N<\begin{matrix}N{=}C\cdot NH_2\\ CO\cdot S\end{matrix}$, formed when the last-described compound is mixed with an excess of carbonyl chloride dissolved in toluene and the mixture kept in a closed vessel with frequent shaking for 48 hours, is a white, amorphous compound almost insoluble in the ordinary solvents, and melts at 250°.

α-Naphthylphenylthiosemicarbazide, $C_{10}H_7\cdot N_2H_2\cdot CS\cdot NHPh$, separates when an alcoholic solution of α-naphthylhydrazine and phenylthiocarbimide (equal mols.) is boiled for a quarter of an hour; it crystallises from benzene or dilute alcohol in white, felted needles, melts at 135°, and is insoluble in water and light petroleum.

α-Naphthylanilidothiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N{=}NHPh\\ CO\cdot S\end{matrix}$, prepared by mixing the last-described compound with an excess of carbonyl chloride dissolved in toluene and allowing the mixture to remain for several hours, crystallises from alcohol in colourless needles, melts at 219°, is very readily soluble in acetone, but insoluble in ether and water.

α-Naphthylanilidodithiobiazolone, $C_{10}H_7\cdot N<\begin{matrix}N{=}C\cdot NHPh\\ CS\cdot S\end{matrix}$, is obtained by gradually adding thiocarbonyl chloride in molecular proportion to a cooled solution of phenylthiocarbimide in benzene (10 parts), and finally heating for a while on the water-bath; it separates from alcohol in small crystals, melts at 255° with decomposition, and is insoluble in water, benzene, and light petroleum.

Ethyl oxalate α-naphthylhydrazide, $C_{10}H_7\cdot N_2H_2\cdot CO\cdot COOEt$, is formed by boiling an alcoholic solution of α-naphthylhydrazine and ethyl oxalate (equal mols.) for two hours, evaporating on the water-bath, collecting the reddish-brown oil, and treating it with ether; the crystals which separate are repeatedly recrystallised from benzene, when it is obtained in small, colourless needles, melts at 163°, and is insoluble in water and ether. It does not react with carbonyl chloride at the ordinary temperature, and when heated with it, a viscid, yellow resin is produced.

The *compounds* $NPh<\begin{matrix}N{=}C\cdot[CH(OH)]_2\cdot C{=}N\\ CO\cdot O\qquad\qquad O\cdot OC\end{matrix}>NPh$ and

$$NPh<\begin{matrix}N{=}C\cdot CH(OH)\cdot CH_2\cdot C{=}N\\ CO\cdot O\qquad\qquad\quad O\cdot OC\end{matrix}>NPh$$

are obtained by heating tartaric and malic diphenylhydrazides (Bülow, Abstr., 1887, 138) with a solution containing an excess of carbonyl chloride in a sealed tube for two hours at 130°; the former melts at 182° and the latter at 199°, and both are insoluble in water.

Paratolylthiocarbazinic paratolylhydrazide,

$$C_6H_4Me\cdot N_2H_2\cdot CS\cdot SH, C_6H_4Me\cdot N_2H_3,$$

separates when carbon bisulphide is added to an ethereal solution of paratolylhydrazine; it is washed with ether and dried in a vacuum, when it melts at 109°. If the last-mentioned compound is heated in a porcelain dish with frequent stirring at 110°, hydrogen sulphide and ammonia are evolved and *paraditolylthiocarbazide*, $CS:(N_2H_2\cdot C_6H_4Me)_2$, is formed; this crystallises from benzene in white leaflets, melts at 121°, and, on heating with alcoholic potash, gives *paraditolylthiocarbazone*, $C_6H_4Me\cdot N_2\cdot CS\cdot N_2H_2\cdot C_6H_4Me$, a colouring matter which is precipitated on acidifying the solution, and when pure forms dark-brown, amorphous flocks; it melts at 105°, and its solutions in ether, benzene, and chloroform show a beautiful red and green fluorescence.

Paratolylazoparatolylthiobiazolone, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N_2\cdot C_6H_4Me\\ CO\cdot S\end{matrix}$, is prepared by dissolving the last-described colouring matter in benzene, dropping in a solution of carbonyl chloride in the same solvent until the colour is destroyed, and evaporating on the water-bath; it crystallises from alcohol in yellow, felted needles, and melts at 170°. The *hydrazo*-derivative, $C_6H_4MeN<\begin{matrix}N=C\cdot N_2H_2\cdot C_6H_4Me\\ CO\cdot S\end{matrix}$, is obtained by suspending the azo-compound in alcohol, adding alcoholic ammonia, and passing a current of hydrogen sulphide for 10 minutes, when it is precipitated after a while in white needles; after washing with water and crystallising from alcohol, it melts at 168°, being reconverted into the azo-compound when its alcoholic solution is boiled with ferric chloride.

Paratolylazotolyldithiobiazolone, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N_2\cdot C_6H_4Me\\ CS\cdot S\end{matrix}$, is formed when thiocarbonyl chloride is added to a solution of paraditolylthiocarbazone in benzene; it crystallises from benzene in red, felted needles, melts at 237—238°, and is insoluble in water. The hydrazo-derivative, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N_2H_2\cdot C_6H_4Me\\ CS\cdot S\end{matrix}$, produced by boiling its alcoholic solution with aqueous ammonium sulphide, forms white leaflets, and melts at 155°.

Paraditolylcarbazide, $CO(N_2H_2\cdot C_6H_4Me)_2$, prepared by boiling paratolylhydrazine (2 mols.) with ethyl carbamate (1 mol.), crystallises from alcohol in rhombic tablets, melts at 201°, and is insoluble in water.

Paratolylazoparatolyl-ψ-thiobiazolone,

$$C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N:N\cdot C_6H_4Me\\ CS\cdot O\end{matrix},$$

obtained by gradually adding the calculated quantity of thiocarbonyl chloride to a boiling solution of the last-described compound in benzene, and heating for an hour, crystallises from benzene in yellow needles, melts at 215°, and is very sparingly soluble in alcohol.

Ethyl oxalate paratolylhydrazide, $C_6H_4Me\cdot N_2H_2\cdot CO\cdot COOEt$, produced by boiling molecular proportions of paratolylhydrazine and ethyl

oxalate in alcoholic solution, separates, on cooling, in leaflets, and when crystallised from alcohol or benzene, melts at 133°.

Ethyl paratolylbiazolonecarboxylate, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot COOEt\\ CO\cdot O\end{matrix}$, is formed by heating the last-described compound with carbonyl chloride (1 mol.) dissolved in benzene, at 100° for an hour; it is very soluble in boiling alcohol, and separates from it in prisms, but is almost insoluble in the cold liquid, and melts at 83°.

Ethyl phenylbiazolonecarboxylate, $NPh<\begin{matrix}N=C\cdot COOEt\\ CO\cdot O\end{matrix}$, is formed by treating ethyl oxalate phenylhydrazide (Bülow, *loc. cit.*) with carbonyl chloride; it crystallises from absolute alcohol in prisms, and melts at 87°.

β-Dinaphthylthiocarbazide, $CS(N_2H_2\cdot C_{10}H_7)_2$, is prepared in the same manner as the above-described ditolylthiocarbazide, from naphthylthiocarbazinic naphthylhydrazide (Hauff, Abstr., 1890, 61); it crystallises from benzene in needles, melts at 137—140°, and is insoluble in water; alcoholic potash converts it into the *carbazone*.

Orthotolylthiocarbazinic orthotolylhydrazide, $CS_2(N_2H_3\cdot C_6H_4Me)_2$, is obtained by adding the calculated quantity of carbon bisulphide to an ethereal solution of orthotolylhydrazine (m. p. 53°), when it separates in white crystals, and is washed with ether; it decomposes at 82°, leaving a residue which melts at 102—103°. *Diorthotolylthiocarbazide*, $CS(N_2H_2\cdot C_6H_4Me)_2$, is formed by heating the last-described compound at 90°, and crystallising the product from dilute alcohol, when it is obtained in small, white, felted needles; it becomes green at 120°, melts at 129—130° with decomposition, and is insoluble in water. Both of the last-described compounds resemble the phenyl derivatives (E. Fischer, Abstr., 1878, 308). *Diorthotolylthiocarbazone*,

$$C_6H_4Me\cdot N_2\cdot CS\cdot N_2H_2\cdot C_6H_4Me,$$

is produced by heating the carbazide with alcoholic potash for 20 minutes, diluting, and neutralising, whereby it is precipitated; it is dissolved in chloroform, and methyl alcohol added, when it separates; when quite pure it melts at 168°, dissolving in concentrated sulphuric acid with a bluish-green colour.

Orthotolylazorthotolylthiobiazolone, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N_2\cdot C_6H_4Me\\ CO\cdot S\end{matrix}$, is formed by slowly adding carbonyl chloride dissolved in toluene to a cooled solution of the last-described compound in benzene (5 parts); after purification, it crystallises from dilute alcohol in reddish-brown needles, melts at 144°, and is insoluble in water. The *hydrazo*-compound is formed by dissolving the azo-derivative in absolute alcohol, adding saturated alcoholic ammonia, and passing dry hydrogen sulphide through the cold solution; it crystallises from absolute alcohol in colourless prisms, and melts at 159—160°.

Orthotolylazorthotolyldithiobiazolone, $C_6H_4Me\cdot N<\begin{matrix}N=C\cdot N_2\cdot C_6H_4Me\\ CS\cdot S\end{matrix}$, is obtained by cautiously adding a solution of thiocarbonyl chloride to one of diorthotolylthiocarbazone in the same solvent cooled by ice; it

forms, when pure, yellowish-red, silky needles, melts at 155°, and is soluble in alcohol, benzene, and ether. The corresponding *hydrazo*-derivative crystallises in colourless, microscopic tablets, and melts at 180—184°. A. R. L.

Quinine Hydrochlorides. By O. Hesse (*Annalen*, **267**, 142—144).—Quinine hydrochloride crystallises in long needles having the composition $C_{20}H_{24}N_2O_2,HCl + 2H_2O$, and also in large octahedra having the composition $2C_{20}H_{24}N_2O_2,HCl + 3H_2O$; the needle-shaped crystals lose their water at 120°, the anhydrous salt melting at 158—160°. The acid salt of the composition $C_{20}H_{24}N_2O_2,2HCl$ is easily prepared by adding the theoretical quantity of hydrochloric acid to a solution of the normal salt; on evaporating at a moderate temperature, the anhydrous salt is partly deposited in needles, partly as a gelatinous mass. F. S. K.

Action of Hydriodic Acid on Cinchonine. By G. Pum (*Monatsh.*, **12**, 582—588; compare Lippmann and Fleissner, this vol., p. 81, and Skraup, this vol., p. 83).—The author has obtained the compound $C_{19}H_{22}N_2O,3HI$ by warming cinchonine (30 grams) with colourless hydriodic acid (150 grams) of sp. gr. 1·7 for four hours on a water-bath. On cooling, a mass of yellow crystals was obtained, and this was further purified by recrystallisation from alcohol. The compound evolves vapours of iodine at 223°, and melts at 230°, whilst, on treatment with alcoholic ammonia, only 1 mol. of hydriodic acid is eliminated (compare Lippmann and Fleissner, Abstr., 1891, 1517). The resulting compound, dihydriodocinchonine,

$$C_{19}H_{22}N_2O,2HI,$$

crystallises from alcohol in nearly colourless needles which turn yellow on exposure to light, melts at 187—190°, and combines with with nitric and sulphuric acids, forming the crystalline compounds $C_{19}H_{22}N_2O,2HI,HNO_3$ and $(C_{19}H_{22}N_2O,2HI)_2,H_2SO_4$ respectively. Alcoholic soda converts dihydriodocinchonine into cinchonine and another base, probably isocinchonine, whilst silver nitrate decomposes it with formation of cinchonine alone. G. T. M.

Sulphonic Acids of Cinchona Alkaloïds. By O. Hesse (*Annalen*, **267**, 138—142).—When quinine, conchinine, cinchonidine, and cinchonine are separately treated with anhydrosulphuric acid, they are first converted into the corresponding iso-bases, and then into sulphonic acid derivatives of the latter.

Isoquininesulphonic acid, $C_{20}H_{23}N_2O_2{\cdot}SO_3H$, is readily soluble in water; the solution is strongly lævorotatory, shows a blue fluorescence, and gives an intense dark-green coloration with chlorine and excess of ammonia. The *platinochloride* is readily soluble; the *aurochloride*, $C_{20}H_{23}N_2O_2{\cdot}SO_3H,HAuCl_4$, is a yellow, flocculent compound.

Isoconchininesulphonic acid resembles the preceding compound in all respects, except that its aqueous solution is feebly dextrorotatory.

Isocinchonidinesulphonic acid, $C_{19}H_{21}N_2O{\cdot}SO_3H$, is dextrorotatory in

aqueous solution; the *aurochloride*, $C_{19}H_{21}N_2O\cdot SO_3H,HAuCl_4$, is a yellow compound, readily soluble in dilute hydrochloric acid.

Isocinchoninesulphonic acid is readily soluble in water; its *aurochloride* has the composition $C_{19}H_{21}N_2O\cdot SO_3H,HAuCl_4 + 2H_2O$.

Quininesulphonic acid, $C_{20}H_{23}N_2O_2\cdot SO_3H$, is obtained in the form of its sulphate, when quinine tetrasulphate is moistened with acetic anhydride; it crystallises in colourless prisms, and is only sparingly soluble in hot water, but more readily in hot alcohol. The air-dried substance contains 1 mol. H_2O, which is expelled at 120°, the anhydrous compound melting at 209°. The *platinochloride*,

$$(C_{20}H_{23}N_2O_2\cdot SO_3H)_2,H_2PtCl_6 + 8H_2O,$$

crystallises in needles.

Cinchonidinesulphonic acid, $C_{19}H_{21}N_2O\cdot SO_3H + H_2O$, prepared in like manner, crystallises in small, colourless needles, melts at 225°, and is only sparingly soluble in hot water and alcohol, and insoluble in ether. The *platinochloride*, $(C_{19}H_{21}N_2O\cdot SO_3H)_2,H_2PtCl_6 + 3H_2O$, crystallises in orange needles. F. S. K.

Crystalline Egg Albumin. By F. Hofmeister (*Zeit. physiol. Chem.*, **16**, 187—191; compare Abstr., 1890, 182; 1891, 476, 1122).—These crystals are practically free from ash if adherent ammonium sulphate which has been used in preparing them is carefully washed away. They have the following percentage composition :—C, 53·28; H, 7·26; N, 15·00; S, 1·09; O, 23·37. W. D. H.

Decomposition of Albumin. By E. Drechsel (*Chem. Centr.*, 1891, ii, 712; from *Arch. Physiol.*, 1891, 248—265).—The author finds that the bases which he obtained from caseïn and described as having the formulæ $C_7H_{12}N_2O_2$ and $C_8H_{14}N_2O_2$ are in fact identical, and that the substance has the formula $C_6H_{14}N_2O_2$. The base is isomeric with diamidocaproic acid, and forms two hydrochlorides, the one containing two, the other only one molecule of hydrogen chloride. The former has a strongly acid reaction on litmus, whilst the latter behaves as a neutral substance. (See also Abstr., 1891, 95.) J. W. L.

Physiological Chemistry.

Nasse's Experiments on the Excitability of Frog Muscle in Salt Solutions. By G. Tammann (*Zeit. physikal. Chem.*, **8**, 685—689).—Nasse found that frog muscle retained its sensibility to electric stimulation longer in a 0·6 per cent. solution of sodium chloride than in stronger or weaker solutions. The same phenomenon occurred in the case of other salt solutions. The author finds that the solutions of various salts most favourable for the preservation of the excitability

are of such strengths that they have equal osmotic pressures. Favourable solutions of other salts have, some greater, some, smaller, osmotic pressures. Probably the excitability is due to a definite turgor in the muscle cells. J. W.

Digestion of Starch by Dogs. By Ellenberger and Hofmeister (*Chem. Centr.*, 1891, ii, 713—715; from *Arch. Physiol.*, 1891, 212—296).—The authors have made a series of experiments with a view of determining the rapidity of the digestion of starch by dogs. The animals (dogs) were fed on known quantities of boiled rice, the percentage of starch in which had been determined, whilst pigs were fed on potatoes, for comparison's sake. At different intervals, after being fed, the animals were killed, and the contents of the stomachs examined for starch, dextrin, and sugar. The results obtained show that the dog digests boiled rice starch much more rapidly than the pig does either potato starch or boiled meat. Moreover, the dog was found to digest the rice starch at first more slowly, and later much more rapidly, than it digests boiled meat. These experiments explain too why hunger is experienced so much sooner after a meal of boiled rice than after a meal of boiled meat.

In none of the eleven experiments in which dogs were fed on rice, could any sugar be detected in the contents of the stomach, and the authors conclude that this is owing principally, on the one hand, to the fact that dogs swallow their food without giving much opportunity for the saliva to pass into the stomach, whilst on the other hand, the food, having been boiled, would contain no diastase; the formation of sugar from starch in the stomach being attributed by the authors to the action of these two ferments.

The acidity of the stomach contents was also determined, and it was found that the left division contained less acid than the middle or right divisions; the amount of hydrogen chloride in the left division was very small. The total acidity of the dog's stomach when fed on cereal food is distinctly greater than that of the horse, the pig, or ruminants. Towards the conclusion of the digestion, the total acidity diminishes again. J. W. L.

The Intake of Iron by the Fœtus. By G. Bunge (*Zeit. physiol. Chem.*, **16**, 173—186).—The small percentage of iron in milk, compared to that in the body of young animals, has led previously (Abstr., 1889, 789) to the conclusion that the fœtus receives a store of iron through the maternal placenta previous to birth. This contention is supported by further analyses. The proportionally large percentage of iron in the fœtus gradually sinks as the animal grows, until it reaches the normal level; after this time, milk is no longer a suitable diet, and unless the milk is supplemented by substances rich in iron, such as vegetables, the animal becomes anæmic. W. D. H.

The Presence of Cystin and Xanthine in the Horse's Liver. By E. Drechsel (*Chem. Centr.*, 1891, ii, 712; from *Arch. Physiol.*, 1891, 243—247).—The author has detected cystin and

another substance in horse's liver. The latter is either xanthine or a substance of the formula $C_{24}H_{20}N_{18}O_{10}$. The author suggests that the changes of the sulphur compounds play an important part in the horse's liver, in support of which theory is mentioned the presence of crystals of sulphur, which he has noticed while separating jecorin. J. W. L.

Variations in Glycolytic and Saccharific Powers of Blood in Asphyxial Hyperglycæmia and Diabetes. Localisation of the Saccharific Ferment. By R. Lépine and Barral (*Compt. rend.*, **132**, 1014—1015).—The authors have previously shown that the glycolytic power of dog's blood is diminished by asphyxia (Abstr., 1890, 1172); they now find that it is altogether destroyed if the asphyxia is extended over at least three-quarters of an hour by supplying small quantities of air to the animal. The saccharific power of both the blood and the urine is diminished under these conditions, although it is increased by rapid asphyxia. The glycolytic and saccharific powers of the blood are increased in the artificial diabetes brought about by the injection of phloridzin into the circulation (Abstr., 1890, 1336), and the saccharific power of the urine is also increased in this state, although in ten cases of natural diabetes it suffered a more or less notable diminution.

The saccharific ferment exists in the serum, and not in the white corpuscles, as is the case with the glycolytic ferment; this explains the ease with which it passes into the urine. Jn. W.

Formation of Glucose and Lactic Acid. By T. Araki (*Zeit. physiol. Chem.*, **16**, 201—204; compare Abstr., 1891, 1125, 1392; this vol., 362).—The claim of A. Dastre to priority in connection with this subject is disputed. W. D. H.

Analyses of Human Milk. By J. Szilasi (*Chem. Zeit.*, **14**, 1202—1203).—The author has analysed 36 samples of human milk, and tabulated the results. As an instance how the milk may vary in quality the following two analyses may be quoted:—*Milk No.* 31: sp. gr. 1·0329; fat, 1·00; sugar, 7·35; proteïds, 1·26; ash, 0·20; total solids, 9·81. The mother's age was 30; she had her fourth child; was of strong constitution, and gave plenty of milk. The child was 8 months old, and its average daily increase in weight was 50 grams. *Milk No.* 35: sp. gr. 1·0318; fat, 4·13; sugar, 7·14; proteïds, 1·99; ash, 0·19; total solids, 13·45. The mother's age was 25; she had her first child; a weak constitution, and but little milk. The child was 20 days old, and its daily increase in weight 20 grams.

The analyses were all done by Ritthausen's process, which the author has slightly modified as follows:—

10 grams of milk is diluted up to 200 c.c., and then mixed with 5 c.c. of solution of cupric sulphate (103·92 grams per litre). Sodium hydroxide (1·018 sp. gr.) is now carefully added until the fluid is almost neutralised. The curdy precipitate which forms contains the fat and the proteïds, and is collected on a weighed filter, washed,

dried at 100°, and weighed. It is then extracted with ether in the Soxhlet's apparatus, dried, weighed, and the fat found by difference. The whole is now again dried, but this time at 125°, weighed, then burnt to ash, and reweighed. The loss in weight (after allowing for the weight of the filter) represents the proteïds. The filtrate, which contains the milk-sugar, is made up to 500 c.c. and in 100 c.c. (= 2 grams of sample) the sugar is estimated by Fehling's solution, the precipitated cuprous oxide being finally reduced to metal by ignition in a current of hydrogen. The ash is estimated by evaporating and burning 10 grams of milk.

L. DE K.

Improvement in Soxhlet's Milk-sterilising Apparatus. By SOXHLET (*Bied. Centr.*, **20**, 718—719; from *Milchzeit.*, **20**, 623—624).—The flask used for sterilising milk is now provided with a kind of india-rubber valve instead of the bored india-rubber stopper, which had to be closed after the flask had been heated the first time with a pieee of glass rod.

A series of experiments made by the author show that samples of milk from various sources are not equally readily sterilised. Completely sterilised milk will remain for six months unchanged, even when kept at 35°; milk which is difficult to sterilise, curdles in three or four days.

Pasture grass is preferable to dry fodder for cows, and when it is used the milk is freer from germs; moreover, the germs which emanate from dry fodder are those which are most difficult to kill, and hence milk infected with them is not readily sterilised. Hay, when employed, should therefore be wetted so that there is no dust from it.

N. H. M.

Putrefaction of Bile. By C. ERNST (*Zeit. physiol. Chem.*, **16**, 205—219).—The antiseptic properties of bile are, if existent, very slight. Bile itself rapidly undergoes putrefaction; and various meat infusions, if mixed with bile, also readily putrefy. The products of such putrefactions were investigated, the most striking result being that those mixtures containing most bile, or bile alone, contained most indole. Further, some experiments appear to show that the source of this indole is the so-called mucin of the bile. The pancreatic juice does not seem to hasten the formation of indole from bile mucin. Further, in the intestine most indole is obtainable from the lower portions, where the bile has acted longest.

W. D. H.

Carbamic Acid. By J. J. ABEL and E. DRECHSEL (*Chem. Centr.*, 1891, ii, 713; from *Arch. Physiol.*, 1891, 236—243).—The authors have found carbamic acid in horse's urine, and, since its presence has previously been observed by Drechsel in the blood of both carnivoræ and herbivoræ, the authors conclude that the conversion of carbamic acid into urea in the case of carnivorous animals must progress much more rapidly than it does in the case of herbivoræ.

J. W. L.

Diamines in Diseases. By E. ROOS (*Zeit. physiol. Chem.*, **16**, 192—200).—Two cases of malaria with dysentery are recorded in

which the stools contained in one case cadaverine, in the other putrescine. The method followed was that adopted by Baumann and Udránzsky (Abstr., 1889, 1024) in their researches. In a third case, no diamines were found. It is, however, regarded as doubtful whether these ptomaïnes are the poisons that irritate the intestinal canal. It seems that the free bases act differently from their salts.

W. D. H.

Peptones in the Blood and Organs of Leucæmic Patients. By R. v. Jaksch (*Zeit. physiol. Chem.*, **16**, 243—254).—In many cases of leucæmic blood, especially where the eosinophile cells are abundant, there is a considerable quantity of "peptone." After death it is always found, and increases as putrefaction sets in. The spleen and liver are also overladen with peptone; but in some cases the normal spleen is also rich in peptone.

The word peptone, as used, appears to include propeptone (proteoses); the methods employed were Hofmeister's (precipitation with ferric acetate) and Devoto's modification of the ammonium sulphate method (Abstr., 1891, 1304). The two methods give corresponding results with exudations and urine, but when applied to the tissues Hofmeister's often gives a positive and Devoto's a negative result.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Distribution of Sugar in Boletus edulis and B. aurantiacus. By E. Bourquelot (*J. Pharm.* [5], **24**, 521—524; compare Abstr., 1889, 740).—Histologically the tissue of the cap of the fungus is a continuation of that of the foot, and the filaments of which it is composed descend into the hymenophore. In the full-grown and freshly-gathered state, the author has shown that *B. edulis* contains trehalose, mannitol, and glucose; whilst *B. aurantiacus* contains trehalose and glucose only. The three portions of the plant indicated above were separately examined, as follows:—Extraction by boiling 90° alcohol, distillation of the solution obtained, concentration of the liquid residue to one-tenth of the weight of the material treated, precipitation of the residue by means of 90° alcohol, filtra-

	B. aurantiacus.			*B. edulis.*			
	Trehalose.	Mannitol.	Glucose.	Trehalose.	Mannitol.	Glucose.	
Foot	5·77	6·29	0·31	24·5	0	0·77	gram per kilogram.
Cap	4·06	3·97	0·37	13·8	0	0·71	
Hymenophore ..	0	0	0	0	0	0	

tion after settling, and, finally, evaporation of the filtered liquor to a syrupy consistency. Trehalose and mannitol readily crystallise; they are drained, washed with 90° alcohol, dried, and weighed. The glucose is estimated in the purified mother liquor by means of copper potassium solution. The results given in the table, p. 519, were obtained. J. T.

Amount of Proteïds in Green and in Etiolated Leaves. Acquisition of Green Colour and Growth of Etiolated Leaves. By W. Palladin (*Bied. Centr.*, **20**, 756—760; from *Ber. deut. bot. Ges.*, **9**, 194—198, 229—232).—No exact comparison of the amount of proteïds in green and etiolated leaves has hitherto been made, the older results (those, for instance, of Karsten, *Landw. Versuchs-Stat.*, **13**, 176) being founded merely on the percentage of total nitrogen. In the author's experiments, the seeds were sown in garden soil, the green plants being exposed to normal conditions, and the etiolated plants grown in large, wooden boxes covered with black cloths. The separation of proteïds was effected by Stützer's method. The leaves (without stalks) were heated to boiling in water containing some alum, and treated in the usual manner with copper hydroxide, &c. Total nitrogen was determined by Kjeldahl's method.

The following table shows the percentage of nitrogen and proteïd nitrogen in the leaves of field beans and wheat:—

	Nitrogen.			
	In fresh.		In dry.	
	Total.	Proteïd.	Total.	Proteïd.
1. *Vicia faba*, 21-day green plants—				
Newer leaves	—	—	9·7	7·1
Older leaves (with 12·7 per cent. of dry matter)	—	—	9·2	6·2
2. *Vicia faba*, 22-day etiolated plants—				
Leaves	—	—	10·3	7·5
Stalks	—	—	7·7	1·8
3. *Vicia faba*, 18-day etiolated leaves	1·94	1·34	—	—
4. „ 16- „ „ „	1·86	1·22	10·5	6·8
Wheat leaves, green 15-day plants (average)	—	0·3188	—	—
Wheat leaves, etiolated 15—16-day plants (average)	—	0·2056	—	—

Tables are also given showing the amount of proteïd and of non-proteïd nitrogen in 100 parts of total nitrogen, and the amount of proteïds in the fresh and dry substances. The results point to the conclusion that etiolated leaves may be divided into two classes, according to the amount of proteïds they contain. Leaves of etiolated plants without stalks are poorer in proteïds than green plants, whilst etiolated leaves of plants with stalks are considerably richer in pro-

teïds than the green leaves. Etiolated stalks are very poor in proteïds. The results thus support the author's theory regarding the reasons of the change of form of etiolated plants. Leaves of *Vicia faba*, rich in proteïds, do not remain in the dark in an undeveloped state for want of organic nutriment. Lessened transpiration gives rise to a very slight taking up of minerals, and this causes the leaves of etiolated plants with stalks to remain undeveloped. Etiolated leaves of wheat and etiolated stalks of *Vicia faba* develop quickly, because, in spite of the small amount of albumin they contain, they are able to acquire from the soil much water containing the requisite minerals.

In order to study the effect of light on etiolated leaves, the leaves (of *Vicia faba* and wheat) were placed on distilled water and solutions of various substances, and kept in diffused light. The bean leaves on distilled water grew very little, and all died without becoming distinctly green. On a cane-sugar solution (10 per cent.), most of the leaves became green in 24 hours, and all within 48 hours; but they grew but little, and died in three days. Aqueous calcium nitrate (0·3 per cent.) alone caused the leaves to die without chlorophyll formation; but with nitrate and sugar together, the leaves became green, grew considerably, and remained healthy more than three days. Wheat behaved quite differently: the etiolated leaves became very soon green when kept in pure water, and the presence of sugar had no effect, clearly because the leaves of wheat contained sufficient carbohydrate. The results point to the following conclusions:—(1.) Chlorophyll cannot be formed without sugar. (2.) The chlorophyll first formed in leaves of germinating plants is formed at the expense of the sugar supplied to them by the seed. (3.) Absence of lime is one reason why etiolated bean leaves do not develop.

N. H. M.

Composition of the Leguminosæ. By L. F. Nilson (*Bied. Centr.*, **20**, 734—736; from *Kongl. svenska landtbruksakad. handling.*, 1—12).—The chemical composition, as regards nitrogenous substances, of 38 kinds of leguminous plants was determined in 50 different samples, and also the composition of 10 plants of various kinds. The amount of digestible proteïds was determined by Stützer's method. The plants of the *Lathyrus* group come first, as containing the most nitrogen and being of the most value for feeding: the large amount of amides in *L. silvestris* makes it necessary that it should be used with care. Both the plants of the *Lathyrus* and *Vicia* orders are much more valuable than the clovers, and it is noteworthy that, among the clovers, red clover by no means holds the first place. *Melilotus alba* and *officinalis*, and *Ervum lens*, are to be compared with the better kinds of *Vicia*, whilst *Orobus niger* and *Pisum arvense* resemble the best clovers. *Lotus uliginosus* approaches more nearly the *Gramineæ*. In the following table, the numbers show percentages in the dry matter:—

	Amides.	Proteïds.	Crude proteïn.	Assimilable.	
				Proteïds.	Crude proteïn.
Lathyrus silvestris	11·21	15·67	26·88	14·21	25·42
„ *sativus*	7·89	15·46	23·35	14·50	22·39
„ *heterophyllus*	7·34	16·13	23·47	14·50	21·84
„ *pratensis*	6·31	17·73	24·04	14·10	20·41
„ *maritimus*	9·99	13·17	23·16	10·56	20·55
„ *palustris*	5·50	14·44	19·94	13·00	18·50
Vicia sativa	9·44	12·85	22·29	11·88	21·32
„ *sepium*	4·91	16·18	21·04	14·51	19·42
„ *villosa*	8·04	12·59	20·63	11·27	19·31
„ *cracca*	4·98	14·88	19·86	13·41	18·39
„ *silvatica*	4·05	15·63	19·68	13·94	17·99
„ *cassubica*	5·98	15·24	21·22	9·69	15·67
„ *pisiformis*	2·69	12·01	14·70	10·98	13·67
Trifolium frangiferum	5·15	12·40	17·55	9·82	14·97
„ *medium*	2·97	13·15	16·12	11·22	14·19
„ *hybridum*	3·24	12·47	15·71	10·85	14·09
„ *repens*	4·22	11·69	15·91	9·30	13·52
„ *procumbens*	2·43	14·59	17·02	10·59	13·02
„ *pratense*	3·12	11·42	14·54	9·61	12·73
„ *arvense*	1·55	13·74	15·29	10·53	12·08
„ *montanum*	0·22	12·63	12·05	10·51	10·73
Medicago falcata	6·35	12·96	19·31	11·69	18·04
„ *lupulina*	5·50	13·65	19·15	12·32	17·82
„ *sativa*	3·65	11·56	15·21	10·74	14·39
„ *silvestris*	4·69	9·08	13·77	7·64	12·33
Astragalus alpinus	6·41	16·89	23·30	15·86	22·27
„ *glycyphyllos*	4·94	12·61	17·55	10·61	15·55
„ *cicer*	4·24	10·73	14·93	9·75	13·95
Anthyllis vulneraria	2·26	9·78	12·04	8·25	10·51
Ervum hirsutum	0·83	12·87	13·70	11·17	12·00
„ *Lens*	5·12	12·54	17·66	11·70	16·82
Lotus corniculatus	2·66	10·91	13·57	8·37	11·03
„ *uliginosus*	1·97	10·53	12·50	6·74	8·71
Melilotus alba	8·35	11·08	19·43	9·86	18·21
„ *officinalis*	6·37	10·95	17·32	9·83	16·20
Ononis arvensis	1·95	12·05	14·00	10·94	12·89
Orobus niger	3·75	13·65	17·40	11·89	15·64
Pisum arvense	4·67	10·92	15·59	10·31	14·98

N. H. M.

Fixation of Atmospheric Nitrogen by Arable Soils. By A. Gautier and R. Drouin (*Compt. rend.*, **113**, 820—825).—The authors point out that as the results of their researches some years ago (Abstr., 1886 and 1887) they came to the conclusion that the lower forms of vegetable life play an important part in the fixation of free nitrogen by soils.

The same series of experiments showed, however, that if the soil was quite free from organic matter, there was an actual loss of total nitrogen, even in presence of the lower forms of vegetation. The fixation of atmospheric nitrogen under the influence of vegetation is, therefore, dependent on the presence of organic matter, and if humus is present a smaller but distinct quantity of free nitrogen is absorbed, even though all vegetation is absent.

The authors hold that, in presence of organic matter, which is essential to their development, the aërobic microbes oxidise the organic matter, whilst, at the same time, they convert a small quantity of the surrounding atmospheric nitrogen into nitric or nitrous compounds. The latter are subsequently attacked by anaërobic microbes, and converted into ammonia and amido-compounds (with possibly some free nitrogen), which would eventually be removed in the drainage water or escape into the atmosphere, were it not that the algæ and other low organisms at the surface of the soil retain them, and use them for the building up of their tissues. The function of the algæ, &c., is to act as magazines for the nitrogen which has been absorbed under the influence of microbes developing in the presence of organic matter.

In the experiments of Schloesing and Laurent (this vol., p. 378), the humus present had already been in the soil, had been subjected to the action of microbes, and, consequently, had, in all probability, become saturated with nitrogen. Moreover, in their experiments, one had not free access to the soil. Hence, doubtless, their failure to observe the fixation of nitrogen, except in presence of algæ, &c.

The authors consider that it has yet to be proved that algæ are capable of absorbing free nitrogen in the absence of microbes and organic matter. C. H. B.

Fixation of Free Nitrogen by Plants. By T. Schloesing Jun., and E. Laurent (*Compt. rend.*, **113**, 1059—1060).—In reply to a note by Gautier and Drouin (preceding abstract), the authors emphasise the facts (this vol., p. 378) that they did not observe any fixation of free nitrogen when the soil was bare, but that they did observe such fixation when the soil was covered with cryptogamous growth. Jn. W.

Fertility of Heavy Loam Increased by Lime. By M. Johnstone (*Bied. Centr.*, **20**, 713; from *Naturw. Rundsch.*, **6**, 322).—The potassium silicate present in heavy loam is liable to be rendered soluble by the action of water and carbonic anhydride, and to be then taken up by the roots of plants, on which it acts injuriously. The beneficial effect of lime depends on its power of liberating the potash (which is of great value to plants) with formation of calcium silicate. N. H. M.

Analytical Chemistry.

A New Desiccator. By W. Hempel (*Zeit. ang. Chem.*, 1891, 200—201).—The author has some time ago explained that, as moist air is lighter than dry air, the practice of having the drying agent at the bottom of the desiccator is objectionable. By placing the drier (sulphuric acid, calcium chloride) as high as possible and above the substance, the drying proceeds rapidly and effectively, owing to circulation of the air. The author has now given a definite shape to his apparatus, which is composed of a glass cylinder fitted with a lid, in the shape of the well-known flycatcher, in which the sulphuric acid is placed. The top part of the lid is provided with an arrangement to connect the apparatus with an air-pump, if desired. To prove the superiority of this desiccator, the author took two watch-glasses of exactly equal size, filled each with 10 c.c. of water, and placed one in an ordinary desiccator and the other in the cylinder of the new apparatus. The result was, that whilst the first lot took nine days to evaporate, the second had dried up in three.

L. de K.

Improvement in Gasvolumetric Analysis. By G. Lunge (*Zeit. ang. Chem.*, 1891, 197—200).—The old-fashioned clamps used to support the author's gasvolumeter soon get worn out, or sometimes break down during the experiments, causing great annoyance to the operator. By the new arrangement this source of failure is eliminated. Figs. 1 and 2 represent the new compound screw and forked



Fig. 1.

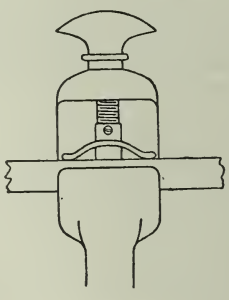


Fig. 2.

clamp; *a* and *b* being respectively a small and large cork-lined clamp, whilst *c* is a species of thumbscrew, shown on a larger scale in Fig. 2.

L. de K.

Simple and Rapid Method of Gravimetric Analysis. By G. H. Bailey and J. C. Cain (*J. Soc. Chem. Ind.*, **10**, 329—330).—A

100 c.c. flask is used, which is made in two parts, the neck being in a separate piece, and accurately ground into the body of the flask. It is desirable to make the neck almost capillary, for the purposes of accurate reading. The flask is first filled with the liquid and precipitate, after which the capillary neck is fitted in, and a little more liquid added, until a given mark on the stem is reached. The latter is graduated in millimetres. These serve, not only to adjust accurately 100 c.c. of liquid at 4°, but also (the capacity of the stem being, once for all, determined) enabled the authors to get rid of the troublesome cooling (or warming) process used in specific gravity determinations. For instance, if the liquid at 4° stood at division 6 for 100 c.c. liquid, and at 10° it stood at division 9, it is evident that when working at 10° the flask must be filled up to division 9, to represent 100 c.c. of liquid at the point of maximum density of water.

Method of Working.—First, the specific gravity of the substance precipitated is carefully determined by ascertaining (*a*) weight of flask and air, and then deducting from this the weight of 100 c.c. of air; (*b*) weight of flask and 100 c.c. of water at 4°; (*c*) weight of flask filled to 100 c.c. mark with water and the substance whose specific gravity was to be determined. The following values were obtained:—

Silver chloride precipitated hot, 5·298.
Silver chloride precipitated in the cold, 5·287.
Copper oxide precipitated hot, 6·514.
Ferric hydroxide precipitated hot, 2·583.
Barium sulphate precipitated hot, 4 651.
Barium sulphate precipitated in the cold, 4·612.

In order to make use of these numbers in the inverse manner for ascertaining the weight of a given precipitate, it is not necessary to replace the supernatant liquor by water, for, by using two similar flasks, 100 c.c. of the clear, supernatant liquor may be run off into one flask, leaving the precipitate and supernatant liquor occupying 100 c.c. in the other flask. Some of the supernatant liquid may also be transferred to a small wash-bottle for washing down any precipitate which remains attached to the sides of the funnel. The actual determination of the weight of the precipitate W now takes this form:—

$$W = \frac{(w' - w)Vs}{Vs - W},$$

where w' = weight of supernatant liquid and precipitate.
w = weight of known volume (say 100 c.c.) of liquid.
s = specific gravity of precipitate.
V = volume of the flask (say 100 c.c.). D. B.

Use of Potassium Hydrogen Tartrate for Titrating Standard Acids and Alkalis. By A. Bornträger (*Zeit. anal. Chem.*, **31**, 43—57).—After giving a summary of most of the methods in use, or suggested, for the standardisation of acid and alkaline solutions, and

pointing out the objections to each of them, the author proposes potassium hydrogen tartrate for the purpose. It is easily prepared and preserved in a pure and definite condition, is anhydrous and not hygroscopic; used directly, it serves as an acid for standardising alkalis, and if ignited it yields a definite quantity of potassium carbonate, by which an acid can be titrated. The author's material was prepared by heating white cream of tartar with dilute hydrochloric acid, cooling with stirring, washing the precipitate completely, recrystallising from water, and drying at 100°. It was regarded as pure when the alkali obtained by calcining a weighed quantity exactly neutralised an equal amount of the uncalcined substance. Sensitive violet litmus-paper was used as indicator. M. J. S.

Gasometric Alkalimetry and the Employment of Potassium Ferricyanide in Gasometry. By J. Quincke (*Zeit. anal. Chem.*, **31**, 1—43).—The reaction $K_6Fe_2Cy_{12} + 2KHO + H_2O_2 = 2K_4FeCy_6 + 2H_2O + O_2$ takes place with quantitative exactness, the amount of oxygen evolved being an accurate measure of the reagent present, so that it can be employed for the estimation of ferricyanides, alkaline hydroxides, or hydrogen peroxide. Assuming that the volume of gas evolved can be read to 0·05 c.c., the error of reading is about equal in magnitude to that involved in measuring a N/10 solution in a burette with float. The potassium hydroxide of the above equation can be replaced by sodium or barium hydroxide with equally accurate results; calcium hydroxide gives results of slightly less accuracy, but still amply sufficient for most purposes. Ammonia is inadmissible, since it decomposes far more of the peroxide than would correspond with an analogous equation. Neither can the alkali or alkaline earthy carbonates be estimated, since they only slowly and imperfectly decompose the peroxide. Weak solutions of the carbonates indeed act so slowly, whilst the reaction with the hydroxides is so rapid (being complete in from one to five minutes), that the presence of a little carbonate does not interfere with the estimation of a hydroxide. The reaction $K_6Fe_2Cy_{12} + BaO_2 = BaK_6Fe_2Cy_{12} + O_2$ also takes place, but not very energetically. By dissolving the barium peroxide in dilute hydrochloric acid, and mixing this solution with excess of strongly alkaline ferricyanide, the reaction becomes rapid and exact.

There are many substances which are oxidised by alkaline solution of ferricyanide, as grape sugar, phosphorous acid, &c.; and, in cases where the products of the oxidation have no action on hydrogen peroxide, an estimation of the residual ferricyanide can be employed for their determination. Arsenious and antimonious trioxides in particular give highly satisfactory results. The potash solution should be strong, and used in large excess. The ferricyanide may be used in the form of standard solution, which, if kept in a bottle of yellow glass, retains its strength for some months. No warming is required. A precipitate of antimony trisulphide may be titrated by dissolving it in concentrated hydrochloric acid, boiling to expel hydrogen sulphide, and then treating the solution with the alkaline ferricyanide. Arsenic trisulphide presents difficulties. The author's

experiments were made with an improved form of Knop's azotometer, in which all parts of the apparatus could be plunged into the same mass of water. The hydrogen peroxide used was "commercial," containing 2 4 per cent. The numerous test analyses reported are highly satisfactory, and tables are given in the paper for facilitating the calculations. M. J. S.

Estimation of Soluble Chlorides, Bromides, and Iodides. By L. L. de Koninck and E. Nihoul (*Zeit. ang. Chem.*, 1891, 294—298).—When a perfectly neutral solution of a chloride, bromide, or iodide (free from barium) is shaken with freshly precipitated silver chromate, the silver combines with the halogen, and the filtrate contains a chromate. The chromic acid may be readily estimated by adding sulphuric acid and potassium iodide, and titrating the liberated iodine with sodium thiosulphate. 3 mols. of this salt or 3 atoms of free iodine correspond with 1 atom of either combined chlorine, bromine, or iodine. Very small traces of chromate may also be estimated colorimetrically. The test analyses are satisfactory.

L. de K.

A New Method for the Estimation of Organic Nitrogen. By J. H. Smith (*Chem. Zeit.*, **14**, 1223—1229).—A preliminary communication as to an indirect process for the determination of organic nitrogen. It is based on the complete oxidation of the organic compound and the conversion of its nitrogen either into nitrogen or nitric acid or both, according to the substance oxidised.

The process is carried out by heating the substance with potassium permanganate, potassium bromide, and sulphuric acid. The amount of the bromide need not be large, as bromine is constantly being regenerated. After cooling, the excess of permanganate is titrated back in the usual manner, after the bromides have been first precipitated with argentic nitrate; and from the difference between the oxygen absorbed in this case, and that absorbed in a like oxidation in absence of bromide, the nitrogen is calculated. L. de K.

Estimation of Nitrogen in Nitrates. By E. Fricke (*Zeit. ang. Chem.*, 1891, 239—241).—A process which the author has successfully employed for some years is as follows:—20 grams of the sample is dissolved in a litre of water, and 50 c.c. is put into a 600 c.c. flask and diluted with an equal bulk of water. 20 grams of potassium hydroxide is now added, and after this has dissolved, 15 grams of zinc and iron dust, also 75 c.c. of alcohol. To prevent frothing, it is as well to add a few granules of animal charcoal. The flask is now closed and connected with a 200 c.c. Peligot's tube which contains 10 c.c. of normal sulphuric acid, and is partially immersed in cold water. After three or four hours, the spirit, which of course carries over the ammonia, is distilled off. The acid is then titrated back with N/4 soda. The process is really an excellent one, provided the potash is free from nitrates. Stützer's process, reduction by means of aluminium wire, cannot be recommended, as the pure metal nowadays, prepared by electrolysis, is far less active than the metal made

by the old process, which yields a product containing both sodium and silicon.

After mentioning Schmitt's process, based on the reduction of nitric acid by hydrogen in acetic acid solution, a process which would be an excellent one if it were not for the frothing and spurting, the author remarks: "This and similar processes must, however, make room for a method lately proposed by Ulsch, which is characterised by simplicity, economy, and celerity." 25 c.c. of a solution containing about 0·5 gram of the nitrate is put into a 600 c.c. flask, and reduced by means of 5 grams of reduced iron and 10 c.c. of dilute sulphuric acid (1—3). To prevent loss by spurting, the flask must be covered with a pear-shaped glass bulb. The liquid is now gradually heated to boiling, and, after six minutes, allowed to cool. After diluting with about 150 c.c. of water, 30 c.c. of aqueous soda is added, besides a few lumps of granulated zinc, and the ammonia is distilled off as usual. On trying this process on a sample of chemically pure sodium nitrate, the author found 16·44 instead of 16·47 per cent. of nitrogen. The process may also be employed for the estimation of nitrates in potable waters. L. DE K.

Estimation of Nitrogen in Pure and Mixed Nitrates. By A. SÜLLWALD (*Chem. Zeit.*, **14**, 1673—1674, 1748).—The author has made several experiments to compare his own process (a modification of Jodlbauer's) with the one recommended by Förster.

The author's process is as follows:—0·5 gram of nitre, or 1 gram of a mixed nitrate, is put into a 150 c.c. flask and moistened with 0·5 c.c. of water. The object of this is to make the nitrate dissolve more easily in the acid, and it also prevents too violent an action. 25 c.c. of sulphuric acid containing 40 grams of phenol per litre is now put into the flask, and, after cooling, 2·5 grams of zinc-dust is added. After waiting for about 15 minutes, a few drops of mercury are added, and the mass gradually heated to boiling. All the nitrogen will thus be converted into ammonium sulphate. The ammonia is then estimated volumetrically as usual.

Förster's process is as follows:—0·5 gram of the nitre is dissolved in 15 c.c. of sulphuric acid containing 6 per cent. of salicylic acid. When the substance has dissolved, 5 grams of sodium thiosulphate is added, and when the action is over, 10 c.c. of pure sulphuric acid and a few drops of mercury are introduced. The conversion of the nitrogen into ammonia is generally accomplished in about 1½ hours.

The results of the experiments proved that the author's process is quite as accurate as Förster's method, although the latter is more simple and is performed in less time. In order to avoid loss, the author recommends treating the nitrate with the acid in the same flask, which is afterwards used for the ammonia distillation. When, however, Chili saltpetre has to be tested, the author prefers his own process to that of Förster, as this substance refuses to properly dissolve in the sulphosalicylic acid. L. DE K.

Estimation of Phosphorus in Iron and Steel. By C. MALOT (*Zeit. anal. Chem.*, **31**, 78—79; from *Compt. rend. mens. de la Soc. de*

l'ind. minér., Avril, 1887).—The phosphorus is precipitated as ammonium phosphomolybdate in the usual way; the precipitate is dissolved in ammonia and reprecipitated by magnesia mixture. The magnesia precipitate is dissolved in nitric acid of 1·2 sp. gr., a drop or two of cochineal tincture (prepared by treating cochineal with boiling water) is added, then ammonia just to violet coloration, which is again removed by one or two drops of nitric acid. There is then added 5 c.c. of a solution containing in the litre 100 grams of sodium acetate and 50 c.c. of acetic acid, the whole is heated to 100°, and titrated with a neutral uranium nitrate solution of known value. As soon as all the phosphoric acid is precipitated, the excess of uranium forms a green lake with the cochineal, so that the colour changes from red to greenish-blue. The uranium solution is of convenient strength if 1 c.c. precipitates 2 milligrams of phosphoric anhydride. Duplicate estimations do not show greater differences than 0·2 milligram.

M. J. S.

Estimation of Phosphorus in Pig Iron, Steel, and Iron Ores. By F. A. Emmerton (*Zeit. anal. Chem.*, **31**, 71—75).—The phosphorus is converted into the yellow ammonium phosphomolybdate, and the amount of the latter ascertained by volumetric estimation of the molybdic acid. 5 grams of steel is dissolved in 75 c.c. of nitric acid (sp. gr. 1·2) in a covered basin, the solution boiled to dryness, and the residue heated for 30 minutes. The cooled residue is taken up by 40 c.c. of strong hydrochloric acid, and the solution evaporated to 15 c.c., taking care that none of the ferric chloride dries on the side of the basin. 40 c.c. of strong nitric acid is now added and again evaporated to 15 c.c., the basin being covered by a clock glass of smaller diameter than itself, placed with the concave side downwards, so that the condensed vapours flowing back prevent the formation of a crust at the edges. A highly concentrated, clear solution free from hydrochloric acid is thus obtained. This is washed into a 400 c.c. flask with about 60 c.c. of water, mixed gradually with a small excess of ammonia, and the precipitate just redissolved by strong nitric acid. The temperature is now brought to 85°, and 40 c.c. of molybdate solution added at once. The flask, stoppered and wrapped in a cloth, is shaken for five minutes, which completes the precipitation. The precipitate is now collected on a suction filter, washed with dilute nitric acid, and then rinsed with 30 c.c. of dilute ammonia through the pierced filter into a flask containing 10 grams of zinc; 80 c.c. of dilute sulphuric acid (1 : 4) is added, and the liquid boiled for 10 minutes, to complete the reduction of the molybdic acid, the colour of the liquid passing through pale-red to olive-green. It is then rapidly filtered and washed through a ribbed filter, and standard permanganate run in until the liquid is perfectly colourless. Since the reduction of molybdic acid by zinc produces a mixture of oxides corresponding with the composition $Mo_{12}O_{19}$, the equation for the titration is $5Mo_{12}O_{19} + 34KMnO_4 = 60\ MoO_3 + 17K_2O + 34MnO$, and since the phosphorus in the precipitate amounts to 1·794 per cent. of the molybdic acid present, a permanganate solution of which 1 c.c. oxidises 0·006141 gram of iron will correspond with 0·0001 gram of phosphorus per c.c.

Pig iron is dissolved in hydrochloric acid, and, after making up and filtering from insoluble matter, an aliquot part is treated as above. Iron ores are dissolved in hydrochloric acid, the solution evaporated to dryness, taken up with hydrochloric acid, concentrated, boiled with nitric acid, then made up, filtered, and an aliquot part of the filtrate employed. M. J. S.

Separation of Phosphoric and Arsenic Acids from Mercury, and of Nitric Acid, Chlorine, and Sodium from Mercury, Phosphoric, and Arsenic Acids. By K. Haack (*Zeit. anal. Chem.*, **31**, 79—81).—1. *Separation of Arsenic and Phosphoric Acids from Mercury.*—If a mercuric salt, the substance is dissolved with hydrochloric acid; if a mercurous salt, it is dissolved in nitric acid with the addition of hydrochloric acid and potassium chlorate, and warming until the odour of chlorine is removed. An excess of ammonia is added, and then, drop by drop, a rather strong solution of potassium cyanide until the precipitate is redissolved. Ammonia is now added until it amounts to one-fourth of the whole volume, and then an equal bulk of absolute alcohol. The arsenic or phosphoric acid can now be precipitated by magnesia mixture in the usual way, and the mercury from the filtrate by hydrogen sulphide.

2. *Nitric Acid from Mercury and Phosphoric and Arsenic Acids.*—The solid substance is boiled for a quarter of an hour with an excess of barium hydroxide. From the filtrate, the excess of barium is precipitated by carbonic anhydride and boiling. The remaining barium is precipitated as sulphate and calculated to nitrate. If alkali metals are present, part or the whole of the nitric acid will remain as alkali nitrate, and, should the alkali be in excess, this method is inapplicable. If otherwise, the alkali must also be determined and calculated as nitrate. For this purpose, the filtrate from the barium sulphate is evaporated, and the residue weighed as alkali sulphate. To separate sodium from mercury and arsenic acid, the substance may be ignited with excess of solid ammonium chloride in a porcelain crucible.

3. *Separation of Chlorine.*—The substance is boiled with baryta as above, and the chlorine estimated in the filtrate. The baryta precipitate is free from chlorine. M. J. S.

Direct Estimation of Arsenic in Minerals and Metals. By J. Clark (*J. Soc. Chem. Ind.*, **10**, 444—445).—In 1867, the author, in conjunction with Esilman, showed that ferric salts decomposed the sulphides of a large number of metals, separating sulphur, and forming a salt of the metal, which was accompanied by the reduction of the ferric salt employed to the corresponding ferrous salt. It occurred to the author to utilise this action for the estimation of arsenic when in the form of sulphide. For this purpose, known quantities of pure arsenic sulphide were distilled with a concentrated solution of ferric chloride in strong hydrochloric acid in an ordinary flask connected with a worm condenser, to the end of which a wide tube was attached which dipped into water. The arsenic was

then precipitated with hydrogen sulphide in the cold, and collected on a weighed filter, with the following results:—

(1.) 5 grams As_2S_3 gave 5·02 = 100·40 per cent.
(2.) 5 grams As_2S_3 gave 4·95 = 99·00 ,,

It is absolutely necessary, in estimating the arsenic in this way, that the hydrochloric acid should be concentrated, and it is always advisable to evaporate down the solution three times with a considerable quantity of strong hydrochloric acid. The ferric chloride decomposes the hydrogen sulphide which would be produced by dissolving the arsenic sulphide in hydrochloric acid, facilitates the solution, and enables the arsenic to be estimated directly.

The author has made numerous experiments with ferric chloride on mixed sulphides of arsenic, antimony, and tin with satisfactory results, and has found this to be the simplest and most trustworthy process for estimating arsenic in antimony ore. It is also applicable for the direct estimation of arsenic in iron and copper pyrites.

D. B.

A New Apparatus for the Estimation of Combined and Free Carbonic Acid. By G. Lunge and L. Marchlewski (*Zeit. ang. Chem.*, 1891, 229—234).—In Fig. 1, which shows the apparatus in its proper proportions, but at about one-ninth of its actual size, A represents the generating flask. If used for the analysis of limestone, soda-ash, &c., it has a capacity of about 30 c.c.; but if required for the estimation of carbonic anhydride in water, or carbon in iron, it must have a larger size. The flask, which is shown on a larger scale in Fig. 2, has a side tube *a*, which is connected with a stop-cock *b* and a funnel *c*; it is closed by means of a ground, hollow stopper, which ends in a rather thin, capillary tube *d*, 35 cm. in length This leads to the side tube of a Lunge's gasvolumeter. The bulb underneath the stop-cock *f* holds about 100 c.c., and is connected with a tube holding another 50 c.c., and calibrated into 0·1 c.c. The Friedrich's stop-cock *f* communicates with the capillary tubes *e* and *g*, which run at a right angle to one another. The tube *g* is connected by means of an india-rubber tube with another capillary tube which terminates in a doubly perforated stop-cock *h*. The latter is connected with the Orsat tube E, which is filled with aqueous potash or soda, and is conveniently supported by the same forked clamp (shown in the figure). All the india-rubber joints, except the one at *e*, are wired. The tube E is also fitted with a soda-lime tube *i*, which prevents the entrance of respiratory carbonic anhydride when the potash is blown up. C is the duction tube, which terminates in a sealed capillary *k*, and D the pressure tube, which should be 3·5 cm. wide; both are supported by the forked clamp *l*. To adjust the apparatus, the temperature and pressure must be, once for all, observed, the great advantage of the instrument over similar ones being that it serves as its own barometer. The gas is expelled from B by raising D; *f* is then closed and D lowered until the distance of its mercury level is over 760 mm. from *f*. D should be lowered sufficiently to cause the mercury to

sink below the bulb in B. D is then made fast, and one must wait a short time to see whether f fits tightly, and if the mercury level in B

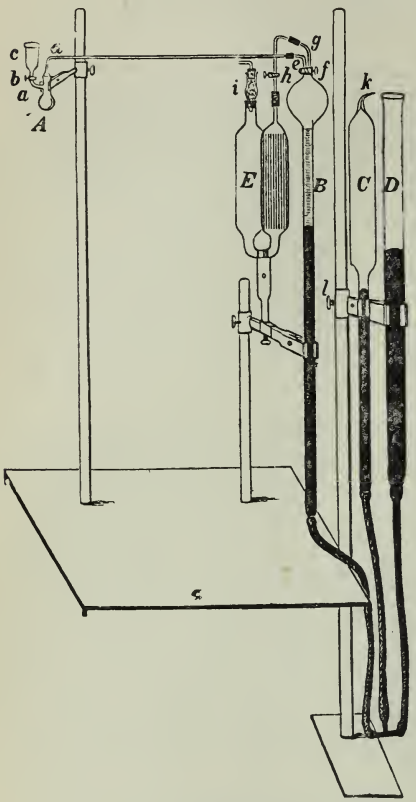


Fig. 1.

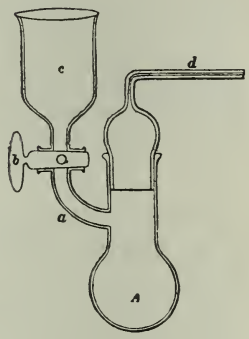


Fig. 2.

remains unchanged. The distance in millimetres between the two mercury levels in B and D is now ascertained by means of any suitable rule. 1 mm. is deducted on account of the tension of mercury vapour at temperatures under 12°, 2 mm. for 13—19°, and 3 mm. for 20—25°, and this corrected pressure is called b. The volume which 100 c.c. of dry air would occupy under these conditions is calculated by the formula

$$\frac{100.(273 + t)760}{273.(b - f)},$$

in which f is the tension of water vapour, which may be taken approximately as $(t - 2)$ for temperatures between 12° and 25°, thus:—

$$\frac{100.(273 + t)760}{273(b - t + 2)}.$$

f is now opened, the mercury in C adjusted to the division corresponding with the calculated volume, and the columns in B and D are brought to the same height. In order to saturate the air with water vapour, a minute drop of water is introduced by means of the capillary K into C. K is now sealed by means of a spirit flame, and, to prevent C getting warm, a screen of cardboard is used. If the mercury still stands at the same division, the apparatus is ready for use, and no corrections need be made for alterations in temperature and pressure.

Before commencing an analysis, it is necessary to conduct a blank experiment to see whether the apparatus is tight. 0·1 gram of fine aluminium wire is introduced into the flask A. B is filled with mercury by raising D, and is made to communicate with A by the stop-cock f, b being closed. D is then lowered, h opened, and D again raised to expel the air in B through E. When this has been repeated about three times, the apparatus is sufficiently exhausted. Hydrochloric acid, diluted with four times its bulk of recently boiled water, contained in the funnel c, is now allowed to run through b into A until this is one-third filled. On applying a gentle heat, a strong evolution of gas sets in, but care must be taken to have the mercury level in D lower than in B. After all the aluminium has dissolved, the stop-cock b is opened, and more acid is allowed to enter until it reaches the neck of the capillary d, and the stop-cock f is then closed. The three tubes are adjusted to the same level, the mercury in C standing at the 100 division, and allowed to remain so for 10 minutes to equalise their temperatures. In the meanwhile, the soda is forced by blowing through i as far as the stop-cock h, which is then closed. A is now detached and cleaned, so as to be ready for the actual analysis. After adjusting, if necessary, the levels of the tubes, the volume indicated by B is read off; f is now turned to make B communicate with g, and h is opened. D is then raised, the gas driven from B into E, and again lowered, which operation is repeated several times. Finally, the soda-ley is again forced up until it reaches h, which is then immediately closed, and the tubes are again brought to the same level, C standing at the 100 division. If the whole apparatus has been air-tight, and the acid been free from carbonic anhydride, the mercury will occupy the same height before and after treatment with the soda.

After driving the gas completely out of B by raising D, the analysis of any carbonate may be performed. An accurately weighed quantity of the substance, together with about 0·8 gram of aluminium, is dissolved in A, as before. The hydrogen completely expels the last traces of carbonic anhydride from the fluid. All the operator has now got to do is to measure the gas both before and after the action of the soda-ley. The difference represents the volume of the carbonic anhydride, which multiplied by 1·966 gives its weight in milligrams. L. DE K.

Apparatus for the Estimation of the Carbonic Anhydride of the Atmosphere. By O. SCHULZ (*Chem. Centr.*, 1891, ii, 726—727;

from *Münchener med. Wochenschr.*, **38**, 641—643).—The apparatus consists of a 500 c.c. cylinder which is graduated for each 20 c.c. At each end it is drawn out. The lower orifice is connected, by means of an india-rubber tube, with a movable reservoir. The upper orifice is closed by a three-way tap. One of the openings of the latter communicates with the air, whilst the other is connected with a stout glass test-tube. The latter is closed by an india-rubber stopper, through one of the holes of which passes a tube drawn out to a capillary at its lower end and reaching to the bottom of the test tube, whilst the other is in connection with the three-way cock of the cylinder. In the test-tube is placed 20 c.c. of a millinormal soda solution, with phenolphthaleïn as indicator. In using the apparatus, the movable reservoir is raised until the water flows from it into the measuring cylinder up to the zero mark, the three-way tap being in connection with the atmosphere. The tap is then reversed so as to come into connection with the test-tube, and the reservoir is now lowered and air allowed to bubble through the soda solution until it is just colourless. The volume of air passed through may then be read off on the cylinder and compared with the weight of carbonic anhydride which exactly neutralises the soda. J. W. L.

Estimation of Calcium in Phosphates by Glaser's Process. By J. H. Vogel (*Zeit. ang. Chem.*, 1891, 357—359).—The author, after carrying out a large number of experiments, has come to the conclusion that the original process recommended by Glaser gives the calcium too low. Excellent results are, however, obtained by using the modified process recommended by Jones (compare this vol., p. 99). Nothing is gained by first drying and separating the calcium sulphate from the filter before calcining it, but too strong a heat should be avoided.

If the phosphate contains much magnesium, there is a danger of this substance coming down with the iron and aluminium phosphates. In this case, Stützer's plan (as explained in Jones's article) must be adopted. L. de K.

Volumetric Estimation of Zinc. By L. Blum (*Zeit. anal. Chem.*, **31**, 60—61).—The author has pointed out (Abstr., 1890, 1191) that in Donath and Hattensauer's method for the titration of zinc, the presence of manganese leads to incorrect results. Moldenhauer prefers to omit the tartrate, and to titrate the zinc in a simple ammoniacal solution, in which the precipitated ferric hydroxide is suspended. If, before making alkaline with ammonia and boiling, a little bromine water has been added to the solution, the manganese will be all precipitated with the iron, and will no longer interfere with the titration of the zinc. Moldenhauer's ammoniacal reagent (5 c.c. for 50 c.c. of solution) consists of 50 grams of ammonium carbonate, 50 grams of ammonium chloride, and 100 c.c. of ammonia in the litre.

M. J. S.

Separation of Copper and Cadmium. By J. S. C. Wells (*Chem. News*, **64**, 294).—Copper and cadmium may be separated, in the absence of ammonium salts, in the following manner:—The

neutral solution containing the two metals is rendered colourless by treating with sodium thiosulphate; the addition of sodium carbonate then precipitates the cadmium as carbonate, which is filtered off. The copper is obtained as sulphide by boiling the filtrate with hydrochloric acid. D. A. L.

Assay of Aluminium and its Alloys. By F. Regelsberger (*Zeit. ang. Chem.*, 1891, 360—363).—Although an experienced dealer can readily distinguish a good sample of aluminium from an inferior one by its appearance and some physical tests, a chemical analysis is more satisfactory. The impurities almost exclusively present are iron and silicon; but it is as well to also make a direct estimation of the aluminium, so as to make sure there can be no other impurities to speak of. The author now recommends the following process:—*Silicon.*—From 2 to 4 grams of cut-up metal is dissolved, with the usual precautions, in 50 c.c. of water containing 12—24 grams of potassium hydroxide. A platinum basin is used, and when the bulk of the metal has dissolved, a gentle heat is applied. The solution is acidified with hydrochloric acid, evaporated to dryness to render silica insoluble, and the residue treated in the well-known manner. *Iron.*—3 grams of the metal is treated in a flask with 50 c.c. of 40 per cent. aqueous potash, and the action assisted by a gentle heat. 200 c.c. of dilute sulphuric acid (1·16 sp. gr.) is now added, and, after boiling to dissolve the iron, the liquid is rapidly cooled and titrated with permanganate. *Aluminium.*—This estimation has already been described (this vol., p. 102).

As regards alloys, the author found that the treatment with aqueous potash completely dissolves out the aluminium from its alloy with 6 per cent. of copper or 20 per cent. of nickel. Even an alloy of aluminium and silver may be so separated, but in this case treatment with nitrohydrochloric acid is preferable. L. de K.

Volumetric Estimation of Alumina. By C. F. Cross and E. J. Bevan (*J. Soc. Chem. Ind.*, **10**, 202).—Lunge (Abstr., 1891, 365) contends that the authors are in error in supposing that the change of colour takes place when the proportion $5SO_3 : 2Al_2O_3$ is reached, the real ratio being $3SO_3 : Al_2O_3$. The authors have repeated their former experiments with precisely the same results. D. B.

Volumetric Estimation of Alumina. By G. Lunge (*J. Soc. Chem. Ind.*, **10**, 314—317).—Referring to the preceding abstract, the author states that he has repeated his former experiments, and has confirmed his results and those of all previous observers, according to which the change in the colour of methyl-orange occurs when $3H_2SO_4$ has been used for $1Al_2O_3$. D. B.

Commercial Assay of Alums. By M. Kretzschmar (*Chem. Zeit.*, **14**, 1223).—Five grams of the sample is dissolved in 500 c.c. of water, 50 c.c. is taken, and the acidity estimated by means of N/2 potash with methyl-orange as indicator. The alumina is then approximately estimated by continuing the titration after addition of phenolphthaleïn. Another 50 c.c. is now taken and boiled with a few drops

of bromine. After cooling, sodium acetate is added, and then a known volume of sodium phosphate of known strength, in order to completely precipitate the alumina and any ferric oxide. As the washing of the precipitate is troublesome and slow, the author prefers to estimate the excess of phosphate volumetrically, in the cold liquid, by means of uranium nitrate solution. As the precipitate also contains ferric phosphate, it is necessary to estimate the iron in another 50 c.c. by reduction with zinc and titration with permanganate. From the amount of alumina obtained by the titration with uranium is then deducted the quantity of alumina corresponding with the ferric oxide.

The process is convenient and rapid. As the amount of alumina is already fairly accurately known by the titration with phenolphthaleïn, the operator knows almost exactly how much uranium will be required to precipitate the excess of phosphate. A single titration will therefore be sufficient. If the alum contains ammonia, the greater part of this must be expelled by heating with excess of alkali. L. de K.

Glaser's Process for the Estimation of Iron and Aluminium in Phosphates. By T. Meyer (*Chem. Zeit.*, **14**, 1730).—A joint committee of German manure makers and agricultural analysts has reported in favour of Glaser's spirit method, instead of the conventional ammonia and acetic acid process. The weak point in Glaser's process is, however, his complete ignoring of the magnesia. Although magnesium sulphate is practically insoluble in absolute alcohol, it is far from insoluble in a mixture of alcohol and dilute sulphuric acid. Manures containing much magnesia always yielded, in the author's hands, a mixture of aluminium, magnesium, and ferric phosphates. Without a serious modification, Glaser's method is therefore not yet fit to become the recognised trade process. (Compare, however, R. Jones, this vol., p. 99.) L. de K.

Estimation of Manganese in its Ores and Alloys. By J. Pattinson and H. S. Pattinson (*J. Soc. Chem. Ind.*, **10**, 333—338).—The authors had occasion to repeat to a certain extent the investigations of Wright and Luff, and of Pickering, on the products obtained by heating hydrated manganese dioxide in air. Their experiments were made with manganosomanganic oxide of known composition, prepared either from crystallised manganese sulphate, or from ferromanganese containing about 82 per cent. of manganese. It is shown that (1) manganosomanganic oxide is only formed from these substances by ignition for about an hour at almost a white heat, in a gas muffle furnace or other apparatus in which the oxide is protected from reducing agents; (2) an ordinary red heat, such as is obtained over a Bunsen burner, is not sufficient to reduce the oxide to the state of Mn_3O_4, and that an error of $1\frac{1}{2}$ per cent. of manganese too much may be made in this way if the percentage of manganese is calculated on the assumption that the product obtained is manganosomanganic oxide; (3) there is a risk in all cases when the oxides are heated over a gas blowpipe of obtaining an oxide containing less

oxygen than Mn_3O_4, probably due to the action of reducing gas permeating the heated platinum or entering the crucible under the lid, and that an error of as much as $3\frac{3}{4}$ per cent. of manganese too little may be made in this way; (4) all determinations of manganese made by weighing the product yielded by igniting manganous carbonate or hydrated manganese dioxide in air are untrustworthy, unless the available oxygen in the product is also determined and taken into consideration.

The authors conclude from their investigations and experience, that, just as in the case of the estimation of iron, the volumetric methods of estimating manganese are far superior to the gravimetric methods, both as regards accuracy and ease of execution. The volumetric method described by one of the authors in 1879 (Trans., 1879, 365), with some slight modifications of detail, is still used by the authors, who have reason to believe that it is now largely adopted by chemists. D. B.

Separation of Metals in Alkaline Solution by Hydrogen Peroxide. By P. Jannasch and R. Niederhofheim (*Ber.*, **24**, 3945—3947).—The method recently described by Jannasch and Franzek (this vol., p. 240) for the quantitative separation of manganese, cobalt, and nickel by treating the alkaline solution of their double cyanides with hydrogen peroxide, may with equal advantage be employed for the separation of manganese and zinc. The solution of manganese and zinc in 50 c.c. of water is mixed with a 10 per cent. solution of potassium cyanide (10 c.c.) and a similar amount of 25 per cent. potash solution, the whole being stirred until the precipitate first formed is redissolved. The manganese is then precipitated by the addition of hydrogen peroxide (50—60 c.c.), the mixture warmed for 15—20 minutes at 100°, and filtered. The filtrate is saturated with hydrochloric acid, evaporated to dryness, warmed at 110—115° in the air-bath for half an hour, dissolved in very dilute hydrochloric acid, and filtered from any silica present. The zinc is then precipitated by sodium carbonate and weighed as oxide.

The analytical data given in the paper show that the method is capable of yielding accurate results. H. G. C.

Action of Alkaline Sulphides on Metals of the Iron Group. By L. L. de Koninck and M. Ledent (*Zeit. ang. Chem.*, 1891, 202—203).—It is a well known fact that when salts of nickel are precipitated with ammonium sulphide in excess, the filtrate has a dark-brown colour, due to some dissolved nickel. According to Lecrenier, this is owing to the ammonium sulphide used for testing nearly always containing polysulphide. The authors thought it would be interesting to try the behaviour of sodium or potassium polysulphide, not only on salts of nickel, but also on the other metals of the same group. Nickel gives a brownish-black, but very clear filtrate, just the same as when using ammonium sulphide. Salts of cobalt give a dirty, violet-brown liquid. With iron, the colour is at first a nondescript dark brown, but gradually changes into a lively green, resembling chromic sulphate or potassium manganate. One

of the authors recommended this reaction some time ago as a delicate test for iron. Manganese salts give no peculiar colour, and, like those of zinc, seem insoluble in an excess of the reagent. The authors will continue the investigation. L. de K.

Estimation of Chromium in Steel. By T. W. Hogg (*J. Soc. Chem. Ind.*, **10**, 340—341).—It has been objected that in Galbraith's process (Abstr., 1877, 357) the whole of the chromium is not dissolved by the sulphuric acid. This objection has most probably arisen from insufficient boiling with the strength of acid originally given (1 to 6), and the author therefore recommends the use of a stronger acid (1 to 3), and to go on boiling the solution vigorously for a few minutes after all decomposition has apparently taken place. The solution should be filtered through an asbestos filter, as with the use of a filter paper a small quantity of chromic acid is reduced. With regard to the gravimetric method of estimating chromium in steel, Arnold's process (Abstr., 1881, 646) gives the best results.

The method recommended by the author is based on the fact that a solution of chrome steel in sulphuric acid is highly coloured, the intensity of the coloration being greater as the percentage of chromium increases. Ferrous sulphate itself has a green tinge, but the colour intensity of chromium sulphate is so very much greater that the presence of even 0·1 per cent. is sufficient to give a decided increase to the depth of colour of the solution, and the presence of 0·35 per cent. will almost double it. D. B.

Gas-volumetric Analysis. By A. Baumann (*Zeit. ang. Chem.*, 1891, 332—339).—Lunge has tried to show that Baumann's new methods of quantitative analyses (this vol., p. 103) do not show any special advantages, and give inaccurate results. The author attempts to prove that Lunge is prejudiced against his process; that, in fact, for the estimation of small quantities of chromic acid and sulphuric acid, no better methods are to be found in the analytical text-books. New gas-volumetric processes for the estimation of arsenious and antimonious acids, and also for the alkalis, will shortly be published. L. de K.

Gas-volumetric Analysis. By G. Lunge (*Zeit. ang. Chem.*, 1891, 339—340).—The author remarks that, nothwithstanding Baumann's pretensions as to the accuracy of his process, he still admits that in the estimation of chromic acid an error may occur of 0·98 per cent., and that in the estimation of sulphuric acid an error of even 1·74 per cent. is possible. The author thinks that more accurate results are obtained by the use of his gas-volumeter than by the azotometer, and points to the fact that his own processes have been used successfully for many years by hundreds of analysts. L. de K.

New Methods in Quantitative Analysis. By A. Baumann (*Zeit. ang. Chem.*, 1891, 203—210, 328—332; compare this vol., p. 103).—The reaction between chromic acid and hydrogen peroxide may be taken advantage of in the estimation of lead, bismuth, and barium. With chromic acid, these metals form insoluble salts, which,

during a quantitative analysis, are generally collected on a weighed filter, and dried at 100—120°. The estimation is, however, much more easily performed by the author's mode of procedure.

Estimation of Lead.—If the liquid should contain free nitric acid, it is first mixed with excess of sodium acetate, then heated to boiling. Potassium dichromate is then added in slight excess. The precipitate is collected and washed, the filter spread out on a glass plate, and the precipitate washed down with dilute sulphuric acid into the outer chamber of the evolution flask. After some time, 5 c.c. of 2 per cent. solution of hydrogen peroxide is added, and the process conducted as previously described. 1 c.c. of gas = 0·0049766 gram of lead oxide.

Estimation of Bismuth.—The solution, which must be free from excess of nitric acid, is poured into a warm solution of potassium dichromate. The precipitate is washed by decantation with hot water, and dissolved in a little weak hydrochloric acid. After transferring it to the evolution flask, and adding 10 c.c. of dilute sulphuric acid, the operation is conducted as in the previous case. 1 c.c. of gas = 0·005192 gram of bismuthic oxide.

Estimation of Barium.—The solution is precipitated with ammonium chromate in the presence of ammonium acetate. The precipitate is washed first with a weak solution of ammonium chromate and finally with very weak ammonia. It is then treated like the bismuth precipitate. 1 c.c. of gas = 0·00342 gram of barium oxide.

The estimations may, of course, also be performed by adding a known quantity of potassium or ammonium dichromate, making up to a definite bulk, and estimating the excess of chromic acid in an aliquot part of the filtrate.

The author has also studied the action of iodine and its oxygen acids on hydrogen peroxide, and obtained results which, if confirmed by other analysts, will revolutionise quantitative analysis. A freshly prepared solution of iodine in potassium hydroxide, which is really a solution of potassium hypoiodite, when brought into contact with hydrogen peroxide, evolves one molecule of oxygen for every molecule of iodine, the products being water and potassium iodide. This fact has been made use of by the author for the estimation of free iodine. 40—50 c.c. of a solution of iodine in potassium iodide is placed in the outer chamber of the flask, and 5 c.c. of 5 per cent. hydrogen peroxide is put into the glass cylinder with a solution of potassium hydroxide (1 : 2). After mixing and shaking, oxygen will be evolved, and after about five minutes' cooling, its volume may be read off. 1 c.c. of gas = 0·01133 gram of iodine. As an instance of the applicability of the method, it may be used to estimate with great rapidity mineral, and even organic, acids, by bringing them in contact with a mixture of potassium iodide and iodate, and estimating the liberated iodine in the manner described. L. de K.

Estimation of Tungsten in Rich Alloys and in Steel. By R. Namias (*Chem. Centr.*, 1891, ii, 728—729; from *Stahl. u. Eisen*, **11**, 757—760).—For the estimation of tungsten in rich alloys, the author prefers to oxidise with bromine in a concentrated sodium hydroxide

or carbonate solution, the finely divided metal being digested in a porcelain dish for 1—2 hours near the boiling point of the solution. The solution is evaporated to dryness several times with hydrochloric acid, the tungstic anhydride is then dissolved from the silica with ammonia, the silica removed by filtration, and the tungstic anhydride again precipitated with hydrochloric acid, and the whole evaporated to dryness. It is then collected, washed with ammonium nitrate solution, and ignited.

The author prefers this method to that of Schneider, by which the tungstic anhydride and silica are fused with potassium hydrogen sulphate. But the mixture of tungstic anhydride and silica may be ignited in a current of hydrogen, and the loss (oxygen) calculated into tungstic anhydride.

In the case of tungsten steel, the metal is digested with hydrochloric acid, in the absence of air, and the insoluble metal collected and washed with ammonium nitrate. A little tungsten passes into the filtrate, and this is recovered by bringing the latter to dryness with hydrochloric acid, sugar is added, and the mass ignited. It is then treated with hydrochloric acid, filtered, washed with hydrochloric acid, ignited, and added to the main portion.

J. W. L.

Analysis of Tin Ores. By J. S. C. Wells (*Chem. News*, **64**, 294).—The author finds that the decomposition of cassiterite can be satisfactorily effected by treating it with dilute hydrochloric acid in the presence of zinc and platinum, heating, and shaking frequently; when the decomposition appears to be complete, the remaining zinc and reduced tin are dissolved in hydrochloric acid and filtered from insoluble matter. The residue is tested for tin, and, if necessary, is treated again. The tin is estimated in the solution by any ordinary method.

D. A. L.

Quantitative Separation of Metals of the Hydrogen Sulphide Group by means of a Stream of Bromine Vapour. By P. Jannasch and P. Etz (*Ber.*, **25**, 124—127; see also this vol., p. 385).—*Separation of Bismuth from Lead.*—A solution of the mixed chlorides is precipitated with hydrogen sulphide, and the precipitated sulphides dried at 100° and heated in a weighed porcelain boat in a stream of air containing bromine. The bismuth bromide completely volatilises, whilst the lead bromide remains behind in a state of purity. The details of the experiments have already been given in a former paper. The special precautions for this separation are, not to allow the precipitated sulphides to remain too long in contact with hydrogen sulphide, and to complete the drying of the sulphides by gently heating them in a stream of dry air before passing the bromine vapour over them. The results obtained were good.

E. C. R.

Application of Electrolysis to Qualitative Analysis. By C. A. Kohn (*J. Soc. Chem. Ind.*, **10**, 327—329).—*Antimony.*—The precipitated sulphide is dissolved in potassium sulphide, and the solution, after warming with a little hydrogen peroxide to decolorise any polysulphides that may be present, electrolysed with a current

giving 1·5—2 c.c. of electrolytic gas per minute, when the antimony is deposited as metal upon the negative electrode. 1 part of antimony in 1,500,000 parts of solution may be thus detected.

Mercury.—This metal is best separated from its nitric acid solution on a small, closely-wound spiral of platinum wire. The solution is electrolysed with a current of 4—5 c.c. The deposited metal is removed from the spiral by heating the latter gently in a test tube, when globules of mercury form on the upper portion of the tube.

Lead.—This metal is precipitated either as peroxide at the anode from a nitric acid solution or as metallic lead at the cathode from an ammonium oxalate solution. In both cases a current giving 2—3 c.c. of gas is sufficient to effect the deposition in one hour. 0·0001 gram of metal in 150 c.c. of solution can be easily detected. With both solutions, this amount gives a distinct discoloration to the platinum spiral, on which the deposition is best effected. As a confirmatory test, the deposited metal is dissolved in nitric acid, and the solution treated with hydrogen sulphide.

Copper.—0·00005 gram of copper can be very readily detected by electrolysing an acid solution in the usual way. A platinum spiral is employed as the cathode, and the presence of the metal confirmed by dissolving it in a small quantity of nitric acid, diluting with water, and adding potassium ferrocyanide.

To detect the above metals in cases of poisoning, it is necessary to destroy the organic matter associated therewith in the usual way by means of hydrochloric acid and potassium chlorate. Urine can, however, be tested directly for these poisons. Mercury or copper may be detected by acidifying the urine with 2—3 c.c. of nitric acid and electrolysing as described. 0·0001 gram of metal in 30 c.c. of urine can be thus detected. Lead does not separate well as peroxide from urine, but if ammonium oxalate be added, the reaction is quite as delicate as in aqueous solution, and 0·0001 gram of lead can be thus detected. Antimony is best detected by precipitation as sulphide and electrolysing with a current of 1·5—2 c.c. In all cases, it is advisable to continue the passage of the current for about twice the time required in the case of aqueous solutions.

Silver.—This metal is precipitated as chloride, dissolved in potassium cyanide, and the solution electrolysed with a current of 1—1·5 c.c. A platinum spiral forms the anode, from which the silver deposit may be dissolved by nitric acid, and tested for by hydrochloric acid or hydrogen sulphide. 0·0001 gram of silver in 150 c.c. can be detected, and one hour is sufficient for the deposition.

Gold is deposited under similar conditions to silver from cyanide solutions. The deposit, which is somewhat dark coloured, can be dissolved in *aqua regia* and tested by the purple of Cassius test. 0·0001 gram of metal in 150 c.c. of solution can be detected without difficulty. D. B.

Separation of Antimony from Arsenic. By F. A. Gooch and E. W. Danner (*Amer. J. Sci.* [3], **42**, 308—312).—A very exact process for the separation of arsenic from antimony consists in distilling their hydrochloric acid solution with ferrous sulphate; but the

conditions are such that the antimony in the residue must be determined gravimetrically. The authors have so arranged the process that the estimation of the antimony may be made by a rapid volumetric method, and this they have accomplished by substituting for the iron salt, which interferes with the direct volumetric estimation, another reducing agent, namely, hydriodic acid. After a great number of experiments, the authors now recommend the following process:—

The solution, which must not contain more than 1 gram of the mixed oxides of antimony and arsenic, is mixed with a slight excess of potassium iodide, diluted with hydrochloric acid to 100 c.c., and then saturated with hydrogen chloride, which is also passed during the subsequent distillation. The apparatus consists of a 250 c.c. flask, provided with a hollow glass stopper tightly fitted in a ground joint, the stopper itself being sealed on a large glass tube bent suitably to connect the interior of the flask with a condenser, whilst through the hollow stopper, and sealed into it, passes a smaller glass tube reaching nearly to the bottom of the flask. By means of this arrangement, a current of gas entering the smaller tube passes nearly to the bottom of the flask, and then out through the hollow stopper into the condenser, without coming in contact with joints, rubber, or cork.

The distillation is continued until fully one-half of the liquid has passed over, when the residue is quickly cooled. Sulphurous acid is added, and, after a little while, the excess of this reagent is destroyed by cautiously adding solution of iodine. After the addition of 1 gram of tartaric acid for every gram of antimony supposed to be present, the free acid is nearly neutralised with sodium hydroxide, and 10 c.c. of a solution of sodium hydrogen carbonate is then added. The antimony is now estimated by titrating the solution with N/10 iodine (compare Gooch and Gruener, this vol., p. 242).

L. de K.

Estimation of Organic Matters in the Atmosphere. By J. Archarow (*Chem. Centr.*, 1891, ii, 887; from *Arch. Hygiène*, **13**, 229—246.)—The author aspirates measured quantities of the air under investigation through a tube, 39 cm. long and 1 cm. wide, which contains solution of potassium permanganate acidified with sulphuric acid. The tube is closed at one end, and fitted, like a wash-bottle, with two tubes, one of which passes to the closed end, whilst the other merely passes through the stopper, and serves as an exit. The inlet-tube is furnished with a cap at its further end, and is perforated so that the bubbles of air are reduced in size as far as may be. Three such tubes are employed in connection with one another for such experiments, and the apparatus is kept warm (about 43°). The potassium permanganate solution has a strength such that 10 c.c. = 0·02 milligram of oxygen, and it is titrated with oxalic acid.

J. W. L.

Apparatus for Determining the Flashing Point of Heavy Mineral Oils. By J. Gray (*J. Soc. Chem. Ind.*, **10**, 348).—The apparatus designed by the author is an adaptation of the Pensky-Marten slide and stirrer to the Abel cup.

D. B.

Indirect Estimation of Alcohol. By T. P. Blunt (*Analyst*, 1891, 221—223).—When alcohol is estimated by the indirect or evaporation method, the spirit gravity is calculated, either by Tabarié's formula, which requires the division of the specific gravity of the sample by that of the extract, or by Mulder's formula, which is based on the assumption that the spirit gravity is obtained by deducting from the gravity of the sample the extract gravity minus 1000. The author has satisfied himself that in the case of sweet wines and liqueurs, the last formula is the most accurate. L. de K.

Estimation of Fusel Oil in Spirits. By J. Traube (*Chem. Zeit.*, **14**, 1410).—The author, in reply to Stützer and Reitmair, still believes his process with the stalagmometer to be the most suitable for analysts who have but seldom occasion to perform a spirit analysis. If it is thought advisable to concentrate the fusel oil, the author operates as follows:—500—600 c.c. of aqueous potash, of 1·24 sp. gr., is put into a suitable vessel, and, after warming to 60°, 100 c.c. of the sample, which must contain 80 per cent. of alcohol, is gradually added. The top layer which forms is removed, and the bottom layer is twice extracted with 20 c.c. of (50 per cent.) pure spirit, in order to remove the last traces of fusel oil. The united spirituous fluids are then tested as usual. L. de K.

Decolorisation of Wines. By A. Bornträger (*Zeit. ang. Chem.*, 1891, 340—343).—Vogel (Abstr., 1891, 1557) has found that most Portuguese red wines require an enormous quantity of basic lead acetate, sometimes three times their volume, in order to render them sufficiently colourless and clear for examination in the polarimeter. The author thinks, however, that as a rule a much smaller quantity will suffice if the sample is first exactly neutralised with potassium or sodium hydroxide, and then concentrated to half its bulk. After addition of the lead solution, the original volume must be restored, and the mixture filtered through a dry filter. Should the reaction be alkaline, this shows that too much lead has been added, and, although it may be remedied by adding a drop of strong acetic acid, it is perhaps better to carefully repeat the whole operation. If the wine is suspected to contain cane-sugar, another portion is first heated for 15 minutes with 10 per cent. of hydrochloric acid, cooled, neutralised, and treated as before. L. de K.

Alkalimetric Estimation of Phenol. By R. Bader (*Zeit. anal. Chem.*, **31**, 58—59).—This can be very accurately effected by the use, as indicator, of symmetrical trinitrobenzene (m. p. = 122°), which substance gives a blood-red coloration with aqueous alkalis. The solution of the indicator is prepared by shaking a pinch of the pure substance with 50 c.c. of absolute alcohol and filtering. It should only be feebly yellow; it requires to be protected from light, and must be freshly prepared from time to time. The phenol solution to be titrated should not contain less than 20 grams in the litre. Only two or three drops of the indicator should be added to 50 c.c. of the phenol solution, and then normal soda, drop by drop, with constant

shaking, until the reddish-yellow colour no longer disappears. 1 c.c. of normal soda = 0·094 gram of phenol. The test analyses leave nothing to be desired.

This method does not seem to be applicable to the cresols, or to catechol. M. J. S.

Estimation of Phenols in Human Urine. By Rumpf (*Zeit. physiol. Chem.*, **16**, 220—242).—The gravimetric estimation of phenol as tribromophenol in the distillate from acidified urine gives most inaccurate results; Koppeschaar-Beckurt's (*Arch. Pharm.*, 1886, 561) method of titration with potassium iodide is trustworthy. Paracresol also cannot be estimated as the tribromo-derivative. The substance obtained by adding bromine to the distillate from urine contains a pigment, and two other substances; one of these, insoluble in sodium carbonate solution, is dibromoparacresol; the other, which is soluble, is tribromophenol; it is, however, present in very small quantities. Hence it is inferred that paracresol is the most abundant substance of the phenol group in the urine. W. D. H.

Estimation of Cholesterol. By J. Lewkowitsch (*Ber.*, **25**, 65—66).—In consequence of the communication of Obermüller (this vol., p. 248), the author publishes the methods he has for some time adopted for the estimation of cholesterol. The first method depends on the quantitative formation of a diacetate of cholesterol when the latter is boiled with acetic anhydride; the precipitate formed is collected, and washed with warm water until no longer acid, its amount being determined by boiling with alcoholic potash of known strength, and titrating back with standard acid. In the second method, which depends on the formation of a di-iodo-additive product, the cholesterol is dissolved in chloroform (50 c.c.), mixed with v. Hübl's solution of iodine and mercuric chloride in alcohol (25 c.c.), and the excess of iodine determined by thiosulphate. Good results are obtained by both methods. H. G. C.

Estimation of Glycerol by Alkaline Permanganate. By W. Johnstone (*J. Soc. Chem. Ind.*, **10**, 203—204).—For the estimation of glycerol in butter fat, the author some time ago recommended the process of Benedikt and Zsigmondy, but although it gives accurate results in certain instances, he now finds it to be quite inapplicable for the estimation of glycerol in butter fat or in oils containing soluble fatty acids. He is, therefore, more inclined to support Wanklyn's statement that the theoretical quantity of glycerol cannot be obtained from butter fat, and that the large amount of soluble fatty acids calculated as butyric acid, recently found by the author, goes a long way to support his "iso-glyceride" theory (compare Abstr., 1891, 849 and 868). D. B.

Analysis of Crude Glycerols. By F. Filsinger (*Chem. Zeit.*, **14**, 1729—1730).—Apart from mixed products, there are three different kinds of commercial glycerol:—1. Saponification glycerol obtained from the works where the fats are saponified with milk of

lime. This brand is characterised by a straw-yellow or brownish colour, has an agreeably sweet taste, and emits no smell when rubbed on the hands. The reaction is generally neutral, unless a trace of free lime should be present. The specific gravity should not be less than 1·24, and its boiling point, in Gerlach's apparatus, not below 138°. The ash should not exceed 0·5 per cent., and neither basic lead acetate nor hydrochloric acid should cause much turbidity.

2. Glycerol intended for distillation, the product of the treatment of fats with sulphuric acid with or without pressure.—This generally has a burning, astringent taste, which often completely obscures the sweet one, an unpleasant odour, and leaves several per cent. of ash consisting chiefly of salt and calcium sulphate. Basic lead acetate causes a voluminous precipitate, sometimes large enough to gelatinise the liquid. Hydrochloric acid often gives a copious fusible precipitate chiefly consisting of fatty matter. The boiling point is generally below 125°. Even the best brands of this glycerol are about 10 per cent. lower in price than the worst saponification glycerols.

3. Glycerol recovered from Soap Leys.—This is the most impure of all, and has to be put through many preliminary processes before it can be distilled. When sold for that purpose, it should not contain more than 10 per cent. of ash and 10 per cent. of water.

As regards the assay of these samples, a chemical one is scarcely needed for the purer kinds of glycerol. All that is wanted is to take the specific gravity with some delicate instrument, and the boiling point in Gerlach's apparatus. As regards the chemical analysis of crude samples, the author recommends the permanganate method, originally described by Benedikt and Zsigmondy, as being the only process which has stood the test of many years' experience.

The author communicates another method which certainly has the merit of being a very simple one, and which has been in use for some years in a Hamburg laboratory. To estimate the water, 20 grams of the sample is put into a flask, provided with a ground stopper, and exposed for 10 hours to a temperature of 100°. The loss represents the water. To estimate the fixed impurities, 5 grams of the sample is heated in a flat-bottomed platinum dish up to 180°, which will cause the glycerol to completely volatilise without perceptible charring. To complete the analysis, the ash may be taken.

L. DE K.

Detection and Extraction of Trehalose. By E. BOURQUELOT (*J. Pharm.* [5], **24**, 524—526).—For the rapid extraction of trehalose from fungi, the plant is treated, as soon as possible after gathering, with boiling 90° alcohol. The solution is distilled, and the residue is concentrated to one-tenth of the weight of fungus employed. The residue, cooled and filtered, is treated with 3 or 4 vols. of 90° alcohol to precipitate certain salts and nitrogenous substances; after filtering and distilling, the residue is evaporated to a rather thick syrup. Now a glass plate is lightly rubbed about its centre with a crystal of trehalose, and a drop of the syrup is placed on the part touched. If the fungus contains trehalose, crystallisation occurs almost immediately, and under a slight magnifying power shows octahedra. A few of these crystals transferred to the syrup will immediately induce

crystallisation in the liquids. In the case where the drop on the glass gives no crystals, trehalose is not present in the extract. J. T.

Estimation of Aldehydic and Ketonic Oxygen. By H. Strache (*Monatsh.*, **12**, 524—532; compare Fischer, *Ber.*, **17**, 572).—Phenylhydrazine and its salts are rapidly decomposed when treated with hot Fehling's solution, the whole of the nitrogen being evolved in the free state; on the other hand, the hydrazones which phenylhydrazine forms with aldehydes and ketones give no free nitrogen when treated in a similar way. On a knowledge of these facts, the author has based a method of determining aldehydic and ketonic oxygen, which is as follows:—A known quantity (0·1—0·5 gram) of the substance under investigation is added to an accurately weighed excess of phenylhydrazine hydrochloride and some sodium acetate, the solution is heated at 100° for several minutes, made up to a known bulk, and an aliquot part withdrawn and heated with an excess of Fehling's solution in a specially constructed apparatus, whereby the nitrogen evolved, representing unchanged phenylhydrazine, may be readily measured, and from this the amount of hydrazine used in forming the hydrazone, and subsequently the amount of ketonic oxygen [$CO:N_2H_3Ph$] present, can be calculated. Determinations with opianic acid, acetophenone, acetone, and several other compounds show that the method is on the whole trustworthy, the results, in most cases, coming out a little too high. The author suggests that the method may, perhaps, be usefully employed in estimating the amount of an aldehydic or ketonic compound present in certain mixtures, and is extending his experiments in that direction. G. T. M.

Separation of Resin from Fatty Acids. By J. A. Wilson (*Chem. News*, **64**, 204—205).—The author regards the following as the best method of detecting resin:—Boil 10 drops of the dry fat or fatty acids with 5 c.c. of acetic anhydride, cool, and add 2 drops of sulphuric acid (sp. gr. 1·84); 1 per cent. of resin is sufficient to produce the reddish-violet colour.

For the separation he strongly advocates the use of Twitchell's process (this vol., p. 389). D. A. L.

Detection of Tartaric Acid in Citric Acid. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 23—24).—The test depends on the fact that the yellow coloration produced by citric acid with ammonium molybdate in presence of hydrogen peroxide is unaltered on warming, whereas, if tartaric acid be present, a fine blue colour results. 1 gram of citric acid is added to 1 c.c. of ammonium molybdate solution (10 per cent.) and 2—3 drops of hydrogen peroxide solution ($\frac{1}{4}$—$\frac{1}{5}$ per cent. H_2O_2), and is heated at 100° for three minutes. The reaction will detect 1 milligram of tartaric acid in 1 gram of citric acid. T. G. N.

Estimation of Uric Acid. By E. W. Groves (*J. Physiol.*, **12**, 485—489).—A comparison between various methods of estimating uric acid leads to the conclusion that Ludwig's is the only trust-

worthy method, and that Haycraft's, with which it was especially compared, gives a very considerable and variable error.

W. D. H.

Revision of Constants employed in the Analysis of Fats and Oils. By R. T. Thomson and H. Ballantyne (*J. Soc. Chem. Ind.*, **10**, 233—237).—In the table of "constants in oil analysis," which accompanies the original paper, will be found collected that portion of the authors' results which they regard as useful in oil analysis.

Iodine Absorption.—In a previous communication (*ibid.*, **9**, 587), it was shown that the variation in iodine absorption for different olive oils was greater than usually stated. Since then, it has been found to be $\frac{1}{2}$ per cent. higher still, so that the iodine value ranges from that of Gioja (79 per cent.) to that of Mogadore olive oil (86·9 per cent.). The lowest figure for rape oil now stands at 99·1, and the highest at 105·6 per cent.

Potash Neutralising Power.—The figures respecting olive and rape oils are in close accord with those obtained by Archbutt, and do not represent such a great variation between each individual oil as those given by other observers. The limits of five specimens of linseed oil examined by the authors vary from 19·00 to 19·28, whilst those of nine specimens tested by other observers and recorded by Allen range between 18·74 and 19·52.

Unsaponifiable Matter.—Olive, refined cotton-seed, unrefined arachis, and linseed oils contain about the same proportion of unsaponifiable matter, so that the determination of that constituent in a sample, say, of olive oil would not serve to show any adulteration with either of the other three oils. But the presence of a considerable proportion of rape oil would tend to reduce the percentage of unsaponifiable matter. In marine oils, it is noteworthy that seal oils contain only about one-third of that contained in whale, cod, and menhaden oils.

Specific Temperature Reaction.—This is merely a modification in recording the results of Maumene's reaction with strong sulphuric acid. It consists in mixing 50 grams of water with 10 c.c. of sulphuric acid, each at 20°, and registering the highest temperature reached. The amount of water is best measured from a pipette at 15·5°, and the sulphuric acid should be run in from a pipette which will deliver the 10 c.c. in one minute. During the addition, the mixture should be vigorously stirred with the thermometer, and the highest temperature reached rapidly read off, as it only remains constant for a few seconds. The oil being tested in precisely the same manner, it is only necessary to divide the rise in temperature obtained with water into that obtained by the oil under examination. The answer is the specific temperature reaction compared with water as 100. The oils must be carefully weighed, and the acid added to them exactly as with water, except that even more vigorous stirring is necessary during and after the addition of acid. In this way, the rise in temperature in all the experiments made by the authors was fairly steady up to the highest point, at which the temperature remained constant for 50 to 60 seconds. In the cases of linseed, cod,

seal, and menhaden oils, the tests had to be made with a mixture of 20 grams of these oils and 30 grams of olive oil of known specific temperature reaction. As a rule, an oil having a high iodine absorption has also a high specific temperature reaction, but the rise is not always directly as that in the former. The reason the specific temperature reaction cannot be depended on with the same assurance as the iodine value is that it shows, in some cases, large variations for the same class of oils.

Valenta's Test.—The authors conclude from the results of their experiments that this test is surrounded with too many conditions to be of any practical value in the general analysis of oils.

Oleïc Acid.—Although the percentage of free acid cannot be looked on as a constant, the authors consider that it serves a purpose in indicating to some extent the condition of the oil, and shows how little, if at all, a high free acidity affects the results of analysis.

D. B.

Detection of Rosin Oil in Fatty and Mineral Oils. By A. Grittner (*Zeit. ang. Chem.*, 1891, 265).—The original process proposed by Storch has only a limited application, as, when sulphuric acid is added to the solution of the oil in acetic anhydride, train oil gives a red colour, whilst with cholesterol, present in many fatty oils, a violet one is produced. With dark-coloured mineral oils, the process fails altogether. Morawsky has modified the process by using a weaker acid of 1·53 sp. gr. Holde also made use of this acid (without the acetic), but of late, he has increased the strength to 1·624 sp. gr., as with the weaker acid the violet-red colour takes a long time to develop. The author found that when mixing rape oil with 1 per cent. of rosin oil, the adulteration may be easily detected by Holde's original or modified process; but Morawsky's method was still more delicate, as it showed $\frac{1}{2}$ per cent. Black rosin oil did not give such a characteristic reaction as was observed with oils of a lighter colour. Train oils, before being tested, must be shaken with alcohol, and the alcoholic solution tested for the rosin oil. The reaction is best observed by allowing sulphuric acid to run down the side of the test tube; if rosin oil be present, a red or violet ring will form at the point of contact. With dark-coloured oils, Holde's method is the best; but with light-coloured train oils, Morawsky's process is preferable. As the reaction is also caused by colophony and shellac, the absence of these substances must be ascertained, and should they be present, it is necessary to saponify the oil and to test the unsaponifiable portion. For dark mineral oils, it is advisable to use an acid of 1·53 sp. gr., as the use of a stronger acid often causes a dark-yellow coloration, which renders the reaction less characteristic. Samples of rosin oil examined by the author gave the reaction with this acid just as plainly as with the 1·624 sp. gr. acid.

Schädler remarks that train oil mixed with syrupy phosphoric acid (5—1) gives a red colour, which gradually turns very dark, and is even noticed in mixtures containing only 1 per cent. of the oil. The author never succeeded in obtaining this reaction, and only noticed a dirty-brown colour. The reaction depends on the nature of the rosin oil. The author occasionally succeeded in detecting

an admixture of 5 per cent., but often could not find it at all. The phosphoric acid process is therefore not to be recommended.

L. DE K.

Estimation of Fat in Milk. By E. GOTTLIEB (*Landw. Versuchs-Stat.*, **40**, 1—27).—The method is a modification of Röse's method (Abstr., 1888, 1135), and is carried out as follows:—A weighed amount of milk (about 10 grams) is poured into a measuring cylinder (40 cm. high), exactly divided into 0·5 c.c. The milk is shaken, first with 10 per cent. aqueous ammonia (1 c.c.), and again, after the addition of alcohol (95° Tralles; 10 c.c.); ether (25 c.c.) is then added. The cylinder is closed with a good cork, which has been wetted, and shaken a few times; light petroleum (25 c.c.) is added, the whole shaken and then left for at least six hours. The volume of the upper layer—a solution of fat in ether and light petroleum—is read, and most of it transferred by means of a fine pipette to a weighed flask, when it is evaporated at a low temperature, the flask and residue dried for 1—2 hours at 100° and weighed. If free from foreign matters, the fat remains as a perfectly clear oil. The weight of fat is calculated to the volume of extract, and to the weight of milk used. The chief difference between the above method and Röse's is that the volumes of milk and alcohol are about the same; the result being that the lower layer has a higher sp. gr., and that the upper layer contains hardly any alcohol.

The method may be further simplified. The milk is measured in a 10 c.c. Geissler pipette, instead of being weighed, and treated as described above. The total volume will be 70·5 c.c.; the upper layer being 53 c.c., and the lower 17·5 c.c. If the pipette used to remove the extract is so adjusted in a cork that it will take out just 51·5 c.c., the weight of residue in milligrams multiplied by 10 will give the percentage of fat in the milk. 10 c.c. of milk weighs 10·33 grams, so that 51·5 c.c. of extract (out of 53 c.c.) corresponds with 10 grams of milk.

With regard to the reagents, normal (or even weaker) potash and soda solutions may be used instead of ammonia. The light petroleum is obtained from commercial petroleum after treatment with sulphuric acid; it boils at about 80°; sp. gr. = 0·671 at 15°. The addition of light petroleum causes the complete separation of the water and a nearly complete separation of the alcohol, as well as the small amounts of matter dissolved in them. This is of much importance, as it is difficult to completely dry fat which contains a little water. The fat is always more or less slightly coloured, according to the feeding of the cow, and when kept readily crystallises. The fat extracted in the usual way is white, and will not readily crystallise. The fat gives no ash when burnt, and is free from nitrogen, and the only foreign substance which could be detected was a small amount of a glyceride of the formula $C_{18}H_{36}O_2$ or $C_{20}H_{40}O_2$, which melts at 75—80°. The milk fat was further examined, and the following results obtained: sp. gr. = 0·936 at 13°; the sp. gr. of fat extracted in the usual manner being 0·943. A determination of the saponification number by Koettstorfer's method showed that 1 gram of the fat required 233 milligrams of

potash, which is near the number obtained by Koettstorfer for pure butter fat. The examination for volatile acids, by Reichert and Wollny's method, showed that, using 5 grams of fat, 28·7 c.c. of decinormal baryta was required; fat obtained by the extraction method requiring 29·8 c.c. The fat showed a normal refractive power.

The results of many analyses made by the method, together with results obtained by Soxhlet's method, and by weighing, show that the method is trustworthy, the results agreeing among themselves even better than those obtained by the other two methods. The method is, moreover, very easily and quickly carried out; the author did 30 analyses in one day, a number which is not to be considered as a maximum.

One advantage in the method is that, owing to alcohol being an antiseptic, the milk, after the addition of alcohol, may be kept in an ordinary bottle for six months before the analyses is completed.

The cylinder employed for the analysis may also be used for estimating fat in cream, butter, and finely-powdered cheese.

N. H. M.

The Lactocrite compared with other Methods for Estimating Fat in Milk. By L. F. Nilson (*Bied. Centr.*, **20**, 789; *Chem. Zeit.*, 1891, No. 37).—The estimation of fat by this process does not always give trustworthy results, especially when more or less of the cream has been removed. This is due to the action of the glacial acetic acid and sulphuric acid mixture on the fat. Good results are obtained by the employment of a mixture of ethylidenelactic acid (90 c.c.) and hydrochloric acid (10 c.c.); the results are then very exact whether the milk is rich or poor in fat.

Kaolin burnt at a high temperature is preferable to pumice, &c., for the absorption of liquids which have to be extracted, and it can always be used again after re-ignition. Adams' method gives concordant and trustworthy results, provided the paper is thoroughly extracted with ether before it is used. The areometric method gives too high results when employed with milk containing under 2·5 per cent. of fat; with milk richer in fat, the results are not uniform, being sometimes too high and sometimes too low. The method is not so good as the gravimetric method (when kaolin or filter-paper are used) or the lactocrite method (compare Abstr., 1890, 1346).

N. H. M.

Milk Analysis. By J. Szilasi (*Chem. Zeit.*, **14**, 1202—1203; see this vol., p. 517).

Soap Analysis. By J. Pinette (*Chem. Zeit.*, **14**, 1442).—The author proposes a simple process for the analysis of soap, which, however, involves the use of Röse's milk fat burette.

The analysis is carried out as follows:—2 grams of the sample is dissolved in boiling neutral alcohol, and any insoluble matter is filtered off and tested if required. The filtrate is mixed with a drop of phenolphathaleïn solution, and if this should cause a reddening, the free alkali is estimated by means of N/10 sulphuric

acid. The liquid is now diluted with water to about 80 c.c. and put into the burette. After cooling, 10 c.c. of normal sulphuric acid is added, and then a mixture of equal parts of ether and light petroleum up to nearly the top division. After thorough shaking, the whole is allowed to remain quietly for some time, and the volume of the two layers is recorded. For the estimation of the fatty acids, 25 c.c. of the ethereal layer is pipetted off and evaporated in a tared basin. If desired, the residue may be dissolved in alcohol and titrated with N/10 alkali. To estimate the combined alkali, 25 c.c. of the aqueous layer is taken, and the excess of acid is titrated with N/10 soda. If the soap is supposed to contain both potash and soda, the alkalis may be weighed as mixed sulphates, and their relative proportion calculated from the sulphuric acid. Allowance must, of course, be made for the amount of soda introduced during the titration. The author claims the following advantages for his process:—The troublesome washing and collecting of the fatty acids is avoided, and there is plenty left of both ethereal and aqueous layers in case of an accident. L. DE K.

Assay of Bees' Wax for Vegetable Wax. By H. RÖTTGER (*Chem. Zeit.*, **14**, 1442—1443, 1473—1474).—The author criticises the various processes from time to time proposed. *Rabineaud's Method.*—1 part of wax is shaken with 50 parts of ether until the mass is thoroughly disintegrated. The insoluble portion is collected on a weighed filter, washed with ether, air-dried, and weighed. If the sample is pure, 50 per cent. remains undissolved; but, suppose it were all vegetable wax, only 5 per cent. of insoluble matter would be found. In regard to this process, Dullo remarks that it is not strictly the case that Japan or vegetable wax is always soluble in ether. There certainly are commercial vegetable waxes which are soluble in ether, but six different samples have been met with which behaved almost like pure bees' wax.

The author repeated the experiment, and tested four samples of Japan wax. Only one gave an unweighable trace of insoluble matter, but the other three completely dissolved in ether. As, however, other wax adulterants, such as stearic acid, paraffin, rosin, tallow, are also soluble in cold ether, the ether test cannot be depended on without further confirmation.

According to Dullo, the best way to test for Japan wax is as follows:—10 grams of the sample is boiled with 120 c.c. of water and 1 gram of soda and potash for *one* minute. If the comparatively easily saponifiable Japan wax is present, a soap is formed, which will more or less solidify on cooling. Pure wax is not affected. The author, however, finds this process to be absolutely useless, as pure wax also gives an emulsion.

According to Hager, Japan wax is sure to be present when the sample, which must be completely soluble in chloroform, has a sp. gr. above 0·980. According to Mène, the adulteration with Japan wax can be detected only by determining the sp. gr., not by taking the fusing or solidifying point.

According to another process by Hager, the fraud is easily detected

by boiling 0·5 gram of borax with 8 c.c. of distilled water and 0·4 gram of the sample. The milky liquid gradually separates into a clear, watery liquid with the wax floating on the top, but when Japan wax is present, it gelatinises more or less. The author tested this process with pure wax, and noticed a clear, watery layer, an emulsion, and a solid mass on the top. In testing for foreign admixtures such as Japan wax, tallow, stearic acid, and rosin, the process is generally very uncertain, as the separation in layers does not always take place as readily as one may think. Stearic acid or rosin may, however, be readily recognised. If the amount of the former is as little as 5 per cent., no solid cake is obtained, but, instead, a pasty emulsion, which, after a few days, separates slightly. In the case of rosin, the liquid also gets pasty, but does not separate at all. The author cannot, however, recommend the process for the detection of tallow or Japan wax, as it will only lead to serious mistakes.

A process lately recommended by the German Pharmacists Association is as follows:—If 1 gram of wax is boiled with 10 c.c. of water and 5 c.c. of sodium carbonate, the wax, after cooling, ought to float on a clear liquid; but if adulterated with Japan wax, stearic acid, or rosin, an emulsion is formed, which, even after remaining for a day, shows no inclination to separate. The author finds that when wax is adulterated with the said substances, or with tallow, a solid cake is obtained, besides an emulsion and a clear liquid. The emulsion is largest when rosin is present, and least in presence of tallow. In conclusion, the author states that by this process, 2 per cent. of Japan wax, stearic acid, or rosin may be detected by the abnormally large emulsion. Tallow does not show well under 5 per cent.

L. DE K.

Salicylsulphonic Acid as a Test for Albumoses and Peptones. By J. A. MACWILLIAM (*Brit. Med. J.*, **1**, 1892, 115; compare Abstr., 1891, 872).—The precipitate produced by adding salicylsulphonic acid to heat-coagulable proteïds (albumin, globulin, myosin, &c.), or to derived albumins (acid-albumin and alkali-albumin) does not dissolve on heating, but becomes coagulated. If it is added to a solution of a primary albumose (proto-albumose or hetero-albumose), the precipitate dissolves on heating, and reappears on cooling. If it is added to a solution of deutero-albumose, this reaction does not take place unless a considerable amount of neutral salt, such as twice its bulk of saturated ammonium sulphate solution, is added also.

True peptone gives no precipitate, unless the solution is fully saturated with ammonium sulphate; the occurrence of this precipitate is stated to be a more delicate test for peptone than the biuret reaction. The precipitate readily dissolves on the addition of a little water or glycerol; it also clears up on heating, and reappears on cooling.

W. D. H.

NO.
A. E. ST
LABO

General and Physical Chemistry.

Electrocapillary Phenomena and Differences of Contact Potential. By Gouy (*Compt. rend.*, **114**, 22—24).—Amalgams containing 0·1 per cent. of zinc, cadmium, lead, tin, or bismuth, or 0·03 per cent. of silver, were compared with pure mercury, the conducting liquid being water acidified with sulphuric acid. In a system consisting of non-polarised mercury, water acidified with sulphuric acid, and a more or less polarised amalgam (0·1 per cent. of foreign metal), the superficial tension of the amalgam is a function of the apparent difference of potential δ between the amalgam and the mercury, and this function remains the same if the amalgam is replaced by mercury. This result is a very close approximation to the truth, although the function is not known for amalgams through so wide a range as for mercury. Adopting the views of Helmholtz, it follows that the difference of contact potential between mercury and amalgams containing 0·1 of the other metal is either *nil* or is very small. Amalgams containing a lower proportion of mercury behave differently. For example, the difference of potential between mercury and a solution of 1 part of Darcet's alloy in 4 parts of mercury is +0·15. C. H. B.

Determination of Vapour Densities under Diminished Pressure. By C. Schall (*J. pr. Chem.* [2], **45**, 134—144).—The method is based on the observation that, if gas be evolved in a uniformly-heated bulb, fitted with a capillary and manometer, the rise in the pressure is independent of the place at which the evolution of gas takes place, and is exactly proportional to the amount of gas or vapour produced if the capacity of the space shut off by the manometer can be considered constant.

The pressure, h, due to the evolution of carbonic anhydride from a known weight of pure sodium carbonate G and dilute sulphuric acid is observed, and also the pressure h', due to the vaporisation of a know weight g' of the substance, whose vapour density is to be determined. The density D is then calculated by the formula

$$\text{I.}\quad D = \frac{g' \times h \times 106 \times 1{\cdot}528}{h' \times G \times 44} = \frac{g' \times h \times 3{\cdot}682}{h' \times G},$$

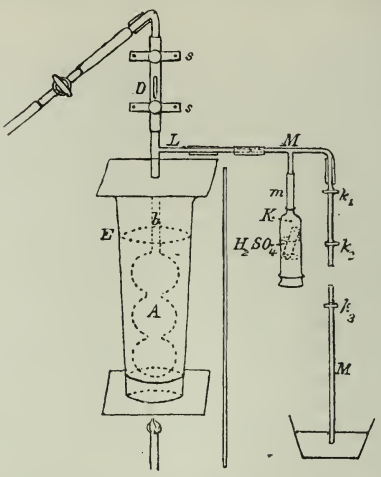
and the molecular weight $M = 28{\cdot}87 \times D$.

$$\text{II.}\quad \therefore M = \frac{g' \times h \times 106{\cdot}3}{h' \times G}.$$

By using equal quantities of carbonate and the substance, g' and G are eliminated from the above equation.

The apparatus consists of a fairly thick-walled bulb A, of about 150 c.c. capacity, twice contracted to hinder the diffusion of the vapour of the substance into the neck b, and fitted with a side tube L. The bulb is connected by means of the tubing D with the air-pump,

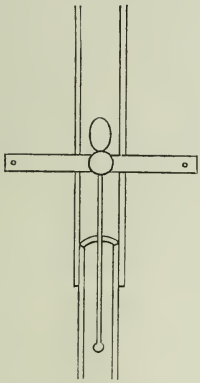
the connecting tube being furnished with a glass tap. s and s' are two screw clips, the upper one to close the apparatus; the lower one



to support the small tube containing the substance whose vapour density is required. The manometer M is 3—4 mm. in internal diameter, and dips into a vessel of mercury, having an area of at least 12—20 cm. The bell-tube K is connected by an india-rubber tube m with the manometer tube, and is closed below by a rubber stopper. It serves for the decomposition of the carbonate. The bulb A is suspended by a clamp in a high, narrow beaker, containing a depth of 3—4 cm. of a liquid, by the vapours of which the bulb can be conveniently heated. The top of the bulb is at about 8—9 cm. from the edge of the beaker, which is covered with a paper or asbestos card. The sides of the bulb are about 5 mm. from the sides of the beaker.

After testing the apparatus to see that it is air-tight and dry, the vapour density determination is performed as follows :—The substance whose vapour density is to be determined, contained in a small tube, is introduced into D, and K charged with the necessary quantity of carbonate and sulphuric acid is fastened in position. The pressure is brought to about 300—400 mm., and the top clip s is closed. Then the third, k_3, of the four rubber rings on M is placed so that its top edge is on a level with the mercury in the manometer. If the level of the mercury remains constant, the bulb is heated by boiling a liquid of known boiling point in the beaker, and the flame so regulated that the height of the vapour of the boiling liquid is constant at the level E. The mercury sinks from k_3, and when its height is constant the pressure is again brought to about 300—400 mm., and marked with k_3. If the mercury level does not keep constant, it is probably due to vapour given off from the substance whose density is to be determined. In this case the substance is put into a small bulb filled as full as possible, drawn out to a capillary point, and suspended in the lower clamp s', as shown in figure; then by bending the rubber tube

the capillary can be broken, and the clip being at the same time released, the substance falls into the bulb. If the level of the mercury is constant at k_3, the acid and carbonate are gradually mixed and



shaken until no more carbonic anhydride is evolved, and the mercury level is again constant. This level is marked with k_4, and the distance between k_3 and $k_4 = h$ is measured. The top clip s is then opened, and the pressure brought to the point at which the substance is to be vaporised. The clip is then shut, the mercury level marked with k_1, the substance allowed to fall into the bulb by opening s', and when the level of the mercury is constant it is marked with k_2, and the distance k_1 to $k_2 = h'$ is measured.

If the decomposition of the carbonate and the vaporisation of the substance take place under the same pressure, then formulæ I and II give correct numbers. But if the decomposition of the carbonate takes place under a higher pressure, the following correction must be made. If Dc is the corrected, and D the density calculated by formula I, then

$$Dc = D\left[1 + \frac{lr^2\pi}{V \cdot \frac{273}{273 + T} + v}\right],$$

when l = distance between k_1 and k_3 in centimeters; r half the internal diameter of the manometer tube in centimeters; $\pi = 3{\cdot}14$; V = volume of the bulb in cubic centimeters; T the temperature of the bulb; v the volume of the capillary bulb to k_1 in cubic centimeters.

If it is necessary to make the determination in an indifferent gas, the latter is led into the apparatus by means of a tube passing through D to the bottom of the bulb, and the air is allowed to escape through M. When all the air is expelled the tube is withdrawn, the substance quickly introduced, and the apparatus connected as before, with the air-pump. E. C. R.

Depression of the Melting Point by Phenol. By Juillard and Curchod (*Bull. Soc. Chim.* [3], **6**, 237—238).—Two values have been

given for the molecular depression of the melting point by phenol: that of Raoult, who gives 67·5 as the result of experiments made with phenol of melting point 37·8° on naphthalene, camphor, benzoic acid, and thymol, and that of Eykman, who gives 76. The authors, in experimenting with a synthetically prepared sample of phenol (m. p. 41·2), found that the molecular depression varies with the solvent substance; for water, β-naphthol, paratoluidine, aniline, nitrobenzene, phthalic anhydride, diphenic anhydride, α-naphthylamine, amyl alcohol, ricinic acid, and salol, the value 68·5 holds, whereas for normal ethereal salts, and particularly those of bibasic acids, such as methyl diphthalate, ethyl succinosuccinate, ethyl malonate, ethyl succinate, ethyl acetoacetate, the value is 75·81. The authors determined the depression in a long-necked, thick glass flask, of 40—50 c.c. capacity, by noting the solidifying point of the phenol after the addition of the other substance. T. G. N.

Absorption of Gases by Liquids. By L. W. Winkler (*Zeit. physikal. Chem.*, **9**, 171—175).—From his own experiments on the absorption coefficients of various gases in water, the author finds that the percentage decrease of the coefficient between 0° and 20° is approximately proportional to the cube root of the molecular weight of the gas, as may be seen from the following table:—

	Percentage decrease.	Cube root of mol. wt.	Ratio.
H_2	15·32	1·259	12·17
N_2	34·33	3·037	11·30
CO.....	34·44	3·037	11·34
NO	36·24	3·107	11·66
O_2.....	36·55	3·175	11·51

The author considers the change in the internal friction of the water to be the real cause of the decrease of the absorption with rise of temperature. If μ and μ_1 represent the internal friction of water, and β and β_1 the absorption coefficients of a gas at two temperatures, then, if m is the molecular weight of the gas,

$$\frac{\beta - \beta_1}{\beta} = \frac{\mu - \mu_1}{\mu} \frac{\sqrt[3]{m}}{k},$$

or

$$k = \frac{\mu - \mu_1}{\mu} \cdot \frac{\beta}{\beta - \beta_1} \cdot \sqrt[3]{m}.$$

The values of k for the gases above mentioned between 0° and 20° are approximately the same. The coefficients of absorption, calculated by means of this constant from the internal friction of water up to 60°, agree very well with the experimental numbers. J. W.

Measurement of Osmotic Pressure. By G. Tammann (*Zeit. physikal. Chem.*, **9**, 97—108).—The osmotic pressure of salt solutions, for example, of potassium nitrate, has been observed to be smaller than that required on the electrolytic dissociation theory of Arrhenius. This the author shows to be due to the fact that the membrane of

copper ferrocyanide, employed in making the observation, is not perfectly impermeable to the salt (or its ions), and thus the osmotic pressure appears smaller than it really is. If the rate of diffusion of the salt through the membrane is determined, a correction may be applied which brings experiment and theory into harmony.

The author points out that the membrane of copper ferrocyanide may be obtained in two modifications. That prepared from dilute solutions of copper sulphate and potassium ferrocyanide is, when fresh, transparent and extremely thin, allows water to pass through it freely, and is extensible like a thin film of rubber. The membrane prepared by allowing the solutions to remain for a long time in contact with each other on the surface of a porous tile, is opaque, dark-brown in colour, much less permeable to water, and very little extensible. The presence of sodium sulphate in the copper sulphate solution conditions the formation of the second class of membrane. Good results are obtained in depositing membranes within porous cells by taking the solutions much more concentrated than those recommended by Pfeffer, namely, a normal solution of copper sulphate and one-third normal solution of potassium ferrocyanide.

A new method of measurement of the osmotic pressure in solutions is proposed by the author. If two solutions having different osmotic pressures are on the opposite sides of a semipermeable membrane, water will flow into the solution with greatest osmotic pressure. This flow may be counterbalanced by subjecting the hyperosmotic solution to external pressure equal in amount to the difference between the osmotic pressures of the two solutions. An osmotic apparatus on this principle is figured and described in the paper; tables of the results obtained are also given. J. W.

Law of Thermodynamical Coincidence and its Application to the Theory of Solution. By L. Natanson (*Zeit. physikal. Chem.*, **9**, 26—42).—According to Van der Waals, if pressure, volume, and temperature are expressed in terms of their critical values, one and the same equation between any of the values will hold for all homogeneous substances. The author constructs orthobaric curves for carbonic anhydride, nitrous oxide, ether, methyl and ethyl alcohols, expressing temperature and volume in terms of their critical values, and finds that under these circumstances the curves do very nearly coincide. The extension of Van't Hoff's theory of solution by Masson (Abstr., 1891, 791) renders it probable, moreover, that the law of Van der Waals applies equally both to solutions and to gases, and Masson has shown that the orthobar for aniline and water resembles that of alcohol. The author, therefore, constructs orthobaric lines for all pairs of liquids for which data are obtainable. These are phenol and water, isobutyl alcohol and water, aniline and sulphur, and allyl-thiocarbimide and sulphur. When the temperatures and volumes are given in terms of their crititical solution values, the orthobars obtained are found to be coincident, and, on comparing the general orthobar for the solutions with that for gases and vapours, the identity of the two is, in spite of certain differences, rendered immediately apparent. H. C.

Organic Liquids as Solvents of Metallic Salts. By A. Étard (*Compt. rend.*, **114**, 112—115).—The percentage solubilities of mercuric and cupric chlorides in various aliphatic alcohols, acids, ethereal salts, ethers, and ketones are plotted out as functions of the temperature, the observations ranging between −60° and +210°.

The curves of solubility of mercuric chloride in water and methyl and ethyl alcohols have the same general character, all three becoming steeper as the temperature rises, and at a definite temperature, which decreases with increase of molecular weight, changing into straight lines of much slighter gradient, passing when produced through the point corresponding with the melting point of the pure chloride. The experiments with water could not be carried above 150°, owing to the dissociation of the salt, of which the solution at that point contained 80 per cent. With propyl alcohol, the whole curve is rectilinear, and the portion below the point of inflexion is not so steep as that above, and this is the case also with acetic acid, whilst with ethyl acetate the solubility between −60° and +40° is constant, the solution containing about 40 per cent. With isobutyl alcohol and with ethyl ether, the observation extends only to a single rectilinear branch of the curve, which, in the case of the latter, has but a very slight gradient. The curve of solubility of mercuric chloride in ethyl formate is a horizontal straight line as far as 48°—the extent of the observations—whilst with acetone the curve is an inclined straight line up to 0°, and horizontal above that temperature.

The curves of solubility of mercuric chloride in isobutyl alcohol and acetic acid tend to pass through the point corresponding with the boiling point of the pure chloride, and thus seem to establish a direct link between the dissolved and gaseous states.

The curves of solubility of brown, anhydrous cupric chloride in ethyl, propyl, isopropyl, and butyl alcohols, and in acetone, and ethyl formate and acetate are in all cases straight lines without points of inflexion; but the observations extend over temperatures ranging only between −15° and +75°. In the cases of allyl alcohol, acetone, and the ethereal salts, the solubility diminishes as the temperature increases.

The curves of constant solubility mentioned above, and first described in a previous note (this vol., p. 397), were found in several instances to correspond with simple molecular relations between the solid and the solvent. Mercuric chloride, for example, dissolves in ethyl acetate between −50° and +35° in, practically, the proportion $2HgCl_2,9C_4H_8O_2$; and copper chloride, again, dissolves in methyl, propyl, and allyl alcohols in proportions represented by $CuCl_2,7MeOH$; $CuCl_2,5Pr^{\alpha}OH$; and $CuCl_2,8C_3H_5{\cdot}OH$. With methyl alcohol, indeed, an actual crystalline compound, $CuCl_2,2MeOH$, may be prepared by heating the solution of the chloride in the cold alcohol; the brown colour changes to green, and the compound is thrown down as a green, crystalline precipitate, which, when redissolved, forms a green solution. This change of colour occurs also with other of the solvents mentioned. Jn. W.

Theory of the Solubility Curve. By C. M. van Deventer and H. J. van de Stadt (*Zeit. physikal. Chem.*, **9**, 43—56).—In this paper,

the authors discuss the question in how far it is possible to deduce a general law for the connection between solubility and temperature. They discuss the differential equations given by Le Chatelier and Van't Hoff for sparingly soluble substances and by Roozeboom for more soluble salts, and find that none of these equations can be integrated so as to yield a general curve of solubility. They show also that Le Chatelier's law of proportionality between the variation in solubility and heat of solution does not hold generally, and can only be applied in a limited number of cases. H. C.

Theory of Residual Chemical Affinity as an Explanation of the Physical Nature of Solutions. By S. U. Pickering (*Ber.*, **24**, 3629—3647).—The author draws attention to objections raised by himself and others against the theory of electrolytic dissociation in aqueous solutions, and to the fact that his own researches all tend to prove the existence of hydrates in such solutions. He offers an explanation of the facts on which the theory of electrolytic dissociation is chiefly based, taking the theory of residual affinity as his starting point, in the hope that in this explanation, which also takes into consideration the existence of hydrates, there may be eventually found a ground for the reconciliation of the physical and chemical theories of solution.

If the units of valency possessed by each atom are regarded as equal in value, residual affinity may be taken as resulting from incomplete saturation of these units when combination takes place between different atoms. In virtue of the residual affinity of the molecule so formed, it will be capable of combining with other molecules also having residual affinity, with the formation of compounds of a more or less definite character. Hence the dissolution of salt molecules in water with the formation of hydrates, and from the difference in the amount and nature of the residual affinity possessed by different substances, their differences in solubility. If the amount of water present is very large, the residual affinity of each salt molecule may be regarded as exercising an influence over that of a large number of water molecules, but its influence on each separate water molecule would be only small. This influence might, therefore, be readily transferred from molecule to molecule in the solution, the salt molecule thus having a certain freedom of motion comparable with that obtaining in the gaseous state. From this follows the application of gaseous laws to dilute solutions.

A salt molecule which, in virtue of its residual affinity, is combined with a number of water molecules, might be incapable of passing through any porous membrane, in consequence of the size of the complex hydrate, although the porous substance might be permeable by molecules either of the salt alone or of water alone. This view explains the behaviour of so-called semipermeable materials, such materials being probably in reality permeable by molecules of the pure solvent or of the pure dissolved substances. The author finds, in fact, by experiment, that if a solution of alcohol and water is put into a porous vessel and this placed, first in pure water and afterwards in pure alcohol, in the first instance water, and in the second instance

alcohol, enters the vessel, but in neither case does any of the solution pass out, although the material of the vessel is obviously permeable by the molecules of either of the substances present in the solution.

In cases where the salt molecules have very great residual affinity, the attraction of the water molecules for the salt may become nearly equal to that of the component atoms of the salt for one another. A nearly equal distribution of the affinities of the components of a solution would thus take place, and the constituent parts of the salt molecule would have a greater freedom of motion than would otherwise be the case. The freedom of motion would enable an interchange of the positive or negative radicles to take place readily under the influence of a determining force, such as an electric current, and would supply the conditions necessary for electrolysis. The conductivity of a solution would therefore depend on the number of salt molecules present in the above condition, and not, as assumed by the dissociationists, on the number of molecules actually present in a dissociated condition. H. C.

Equilibrium of Double Salts of Lead and Potassium Iodides with their Aqueous Solution. By F. A. H. Schreinemakers (*Zeit. physikal. Chem.*, **9**, 57—77).—This investigation was undertaken with the object of testing the deduction made by Roozeboom from Gibbs' rule for equilibrium between several phases, in the special case of the equilibrium of double salts with their solutions (compare Abstr., 1888, 1147 and 1164). The deductions of Roozeboom have been in every way confirmed. The double salt of lead and potassium iodides crystallises with $2\frac{1}{2}$ mols. H_2O. When brought into contact with water, it can behave in three different ways:—Below 144°, it deposits lead iodide; between 144° and 203°, it is soluble without decomposition; and above 203°, it deposits potassium iodide. At 203°, the solution still contains more than $2\frac{1}{2}$ mols. H_2O, and the melting point of the salt is not yet reached. No dehydration seems to take place below 203°. This salt is remarkable as being the first double salt which has been found to dissolve between wide limits of temperature without decomposition. H. C.

Solubility of Mixed Crystals. By W. Nernst (*Zeit. physikal. Chem.*, **9**, 137—142).—The author applies the osmotic pressure theory to the discussion of the solubility of mixed crystals, which, after Van't Hoff, he treats as solid solutions. He develops equations for the case of isomorphous salts with water as solvent, in which case, of course, electrolytic dissociation has to be taken into account. An application to Roozeboom's observations (this vol., p. 266) on the solubility of thallium chlorate containing potassium chlorate leads to the conclusion that the molecules of the latter substance, in the mixed crystals, must be mostly $KClO_3$; and that the maximum external work obtainable from the expansion by a definite fraction of its volume of a gram-molecule of potassium chlorate in dilute solid solution in thallium chlorate is approximately the same as that obtainable from the expansion of a perfect gas at the same temperature by the same fraction. J. W.

Maximum Tension with which Hydrogen is set free from Solutions by Metals. By G. Tammann and W. Nernst (*Zeit. physikal. Chem.*, **9**, 1—11).—When a metal is brought into contact with an aqueous solution, it frequently happens that the metal dissolves, and an equivalent amount of hydrogen is liberated. This reaction is attended by a considerable increase in volume, and, according to the known laws of the influence of pressure on chemical change, it should be possible by applying a sufficiently great pressure to bring about a reversal of the reaction, and precipitate the metal by forcing compressed hydrogen into the solution. There will, however, also be a particular pressure for which the solution of the metal and hydrogen will be in equilibrium with one another, and this pressure may be termed the maximum tension of the liberated hydrogen. This pressure is a measure of the maximum work obtainable by dissolving metals in acids, and since the E.M.F. of so-called reversible cells is a measure for the same quantity, it follows that the above maximum tension is intimately related to the E.M.F. of reversible cells.

If p is the maximum tension, and P the atmospheric pressure, the work which could be obtained from 2 grams of hydrogen by liberation and transference from pressure p to pressure P would be $A = pv + RT \log \frac{p}{P}$, or if the volume is taken in litres and the pressure in atmospheres, $A = 0{\cdot}0819\,T\,(1 + \log \frac{p}{P})$. Therefore the work which could be obtained from a Daniell cell by the dissolution of a gram-molecule of zinc and the precipitation of a gram-molecule of copper is $A_1 - A_2 = 0{\cdot}0819\,T \log \frac{p_1}{p_2}$. This work is equal to the E.M.F., and introducing the ordinary units of measurement we get the expression $0{\cdot}430\,T \times 10^{-4} \log \frac{p_1}{p_2}$ volt for this quantity, containing the directly measurable quantities p_1 and p_2.

In order to test the above relation, the authors endeavoured to measure the pressures under which hydrogen ceased to be evolved from solutions of metals in acids. The experiments were, however, only partially successful, and do not afford definite confirmation of the theoretical deductions. H. C.

Colour and Constitution of Compounds. By M. Schütze (*Zeit. physikal. Chem.*, **9**, 109—136).—The author has studied a large number of coloured compounds, both organic and inorganic, with view to tracing relations between their colour and constitution. His results may be summed up in the following rules:—

1. The passage of absorption from violet to red in the spectrum usually conditions the following changes of colour: greenish-yellow, yellow, orange, red, reddish-violet, violet, bluish-violet, blue, bluish-green, &c. Going through the colours in this order is called "lowering the tint" by the author; in the opposite order, "raising the tint."

2. Definite atoms or groups of atoms on entering a molecule cause, for compounds of the same chromophore in the same solvent, a

characteristic rise ("bathochromic groups,") or fall ("hypsochromic groups"), of the tint.

3. The hydrocarbon radicles are always bathochromic; consequently in homologous series the shade always deepens as the molecular weight rises.

4. The same is observed in the periodic groups of the elements as the atomic weight increases.

5. Addition of hydrogen causes a raising of the tint.

6. The rise or fall of the tint by substitution of hypsochromic or bathochromic groups, or by addition or loss of hydrogen, is the greater, the nearer the atoms affected by the chemical action are to the chromophore. Judging by this rule the substituents in the para-position in di-derivatives of benzene would sometimes appear to be nearer to each other than substituents in the meta-position.

7. These rules are only valid for monochromophoric compounds, and for such dichromophoric compounds as have two similar active groups influenced by neighbouring atoms in the same way. The colour of an asymmetrical diazo-compound, Y·A·X·A·Z, is approximately the same as that of a mixture of the two symmetrical compounds, Y·A·X·A·Y and Z·A·X·A·Z. J. W.

Tabular Expression of the Periodic Relations of the Elements. By H. Bassett (*Chem. News*, **65**, 3—4, 19).—The author has devised a tabular arrangement of the elements, which he urges removes some of the anomalies of Mendeléeff's table.

Lecture Experiments on the Diffusion of Gases. By H. Biltz (*Zeit. physikal. Chem.*, **9**, 152—157).—An arrangement is described by means of which a glass bulb containing bromine may be broken on the bottom of a covered glass cylinder filled with hydrogen. The bromine vapour diffuses upwards into the hydrogen much more rapidly than it does in a similar cylinder filled with air.

There is further the figure and description of an apparatus designed to show the diffusion of hydrogen through a red-hot iron tube, which is impervious to other gases. The diffusion is indicated by a manometer registering the pressure within the iron tube. J. W.

Oxy-hydrogen Gas. By V. Meyer (*Ber.*, **24**, 4233—4243).—The author describes with the aid of cuts a series of lecture experiments illustrative of the various ways in which combination of the hydrogen and oxygen in electrolytic gas can take place.

A stout glass cylindrical vessel, 9 cm. long and 3 cm. wide, having a tube of 2 mm. diameter and 22 cm. in length attached to one end, is filled with electrolytic gas; a portion of the gas, a few cm. from the end of the tube, is aspirated with the mouth by a capillary tube, and the end, thus filled with air, then quickly sealed in the blowpipe. The cylinder is now held in a horizontal position by a clamp and heated by a Bunsen's burner, two plates of glass being placed on either side of it for the protection of the lecturer and audience. The explosion takes place at the temperature at which the glass commences to soften, and is accompanied by loud detonation, the vessel being

sometimes shattered, but frequently only bulged out or drawn in at the heated portion; the point of the tube is, however, always broken off by the explosion.

If some platinum wire of such a thickness that 10 cm. weighs 0·066 gram be placed in a cylinder at each end of which capillary tubes are attached, these being subsequently sealed in the blowpipe, on heating the cylinder as above, the platinum wire suddenly glows, a flame vibrates within the cylinder, and combination takes place almost silently, and at a temperature much below that at which the glass softens.

When glass cylinders provided with capillary ends are filled with pure electrolytic gas, and after fusing the ends, heated in the vapour of boiling phosphorus pentasulphide for 1—2 hours, and the ends then broken off under water, the quantity of entering water shows the amount of combination of the gaseous mixture which has taken place (see *Annalen*, **264**, 85; Abstr., 1891, 1153).

It has been shown by the author and Krause (*loc. cit.*) that the temperature of explosion of electrolytic gas lies between 518° and 606°; if one of the last-mentioned cylinders, filled with the gas and sealed, be held by one of the capillary tubes in the hand, which is protected by a glove, and then plunged into boiling zinc chloride, combination takes place with the production of flame, but without detonation; the cylinder is not injured, but the point of the capillary tube is frequently shattered off. For the success of this experiment, it is necessary that the zinc chloride should be in violent ebullition, and it is best heated in a thin sheet-iron vessel, with a "No. 15 burner," together with the point of the blowpipe flame. When electrolytic gas is passed in a stream through a cylinder surrounded by boiling zinc chloride, only slow combination of the gaseous mixture occurs, and this is accompanied by a cherry-red glow, which is best observed in a dimly-illuminated room.

The influence of foreign substances on the combination of oxygen and hydrogen in the mixture is seen by the following experiments:—A cylindrical glass vessel, with tubes at each end, is coated with silver on its inner surface, and after thoroughly cleaning and drying, capillary tubes are attached to the ends; it is then filled with electrolytic gas, the ends sealed, and the cylinder suspended in boiling aniline vapour for two hours, when combination to the extent of about 90 per cent. of the contained gas is found to have taken place; whilst when a similar experiment is carried out in an unsilvered glass vessel, no combination whatever is found to have occurred. The author promises further details as to the temperature of combination of oxygen and hydrogen in electrolytic gas in a paper to be published in the *Annalen* in conjunction with Askenasy. A. R. L.

A Lecture Experiment. By T. Wilm (*Ber.*, **25**, 217—219).—The occlusion of hydrogen by palladium can be very conveniently shown in the following manner:—A glass U-tube, on the bottom of which is blown a small bulb, intermediate between the two limbs, is connected by one limb, which is bent at right angles near the top, with a drying bottle, through which hydrogen from a Kipp's appa-

ratus is passing; on the other limb is fastened a good, glass stop-cock by means of thick-walled, india-rubber tubing, diffusion being prevented as much as possible by bringing the two glass surfaces into contact. Palladium sponge (3 to 4 grams) having been placed in the bulb of the U-tube, the metal is first heated in a stream of dry hydrogen, and then the whole tube is carefully warmed with an ordinary burner, in order to expel any water that may be formed. If, after the air has been expelled, and while the palladium is still hot, a light is applied to the hydrogen escaping from the stop-cock, a small, intermittent flame is produced; only by almost closing the cock and turning on a rapid stream of hydrogen is it possible to obtain a small, steady flame. After the palladium sponge has been heated a little more strongly, but still far below a red heat, for a short time longer, the heating is discontinued and, after a few seconds, the stop-cock is closed. The occlusion of the hydrogen then commences; the hydrogen streams through the wash-bottle into the air-tight U-tube, and continues to do so for some minutes, until it ceases to be absorbed. If, now, the stop-cock is opened and the palladium again heated, the stream of hydrogen from the Kipp's apparatus remaining as at the commencement of the experiment, the escaping gas can be ignited at the stop-cock, and will burn with a large, steady flame, which, however, immediately becomes smaller, and quickly goes out if the heating of the palladium is discontinued.

F. S. K.

Inorganic Chemistry.

Complex Salts of Sulphurous Acid. By K. Barth (*Zeit. physikal. Chem.*, **9**, 176—219).—Röhrig and Schwicker have prepared two isomeric salts, $Na\cdot SO_2\cdot OK$ and $K\cdot SO_2\cdot ONa$, the former with two molecules of water of crystallisation, the latter with one. When these salts are dissolved in water, the solutions obtained are identical, and have in particular the same conductivity. This follows as an immediate consequence of the theory of electrolytic dissociation, for, according to it, the two salts should give the same products of dissociation in dilute solutions, namely, $\overset{--}{SO_3}$, $\overset{+}{K}$, and $\overset{+}{Na}$.

The double sulphites containing mercury as one of the metals, do not give the ordinary reactions of mercury salts; and Divers and Shimidzu pointed out that they were probably to be considered as salts of a mercury sulphonic acid $Hg(SO_3R')_2$. The electrolytic conductivity and the freezing point of their solutions confirm this view, all the evidence pointing towards a dissociation into three ions R′, R′, and HgS_2O_6.

The author has investigated in detail many cases of double compounds of the mercury sulphonates with other salts. These he finds to be for the most part complex salts, which in solution yield ions containing constituents derived from both the simple salts from which the compound is formed.

J. W.

Metallic Borates. By A. Ditte (*Compt. rend.*, **114**, 71—72).—A discussion with Le Chatelier on a question of priority (see this vol., p. 404). C. H. B.

Carbon. By W. Luzi (*Ber.*, **25**, 214—219).—A peculiar form of carbon can be obtained by heating a porcelain crucible, or crucible cover, in a Fourquignon-Leclercq's blast oven to the highest possible temperature (about 1770°), and then allowing a very smoky flame to play against the white-hot porcelain for 10—15 minutes; if the porcelain is unglazed, it has by this time become covered with graphite, but if glazed, it is coated with a light, lustrous deposit, hardly to be distinguished from a silver mirror. Some portions of this deposit adhere to the porcelain so tenaciously that they can be polished with a cloth; others become detached in the form of mirror-like facets of high lustre. If the loosened portions are pulled off, they curl up into rolls, similar in appearance to metal shavings; these rolls of carbon are exceedingly light, and stick to the fingers and other objects just like silver leaf does. This lustrous form of carbon is free from ash, and seems also to be free from hydrogen; it does not give the nitric acid reaction of graphite (this vol., p. 406), and is quite opaque.

The author has examined 17 varieties of naturally occurring "graphite;" nine samples gave the nitric acid reaction of true graphite, and eight samples did not; the latter must therefore be regarded as graphitite. The grey carbon, obtained by strongly heating the diamond in absence of air, does not give the graphite reaction. F. S. K.

Action of Carbon on Sodium Sulphate in Presence of Silica. By Scheurer-Kestner (*Compt. rend.*, **114**, 117—120).—In the preparation of glass or soluble silicates from alkali sulphate, silica, and carbon, the proportion of the latter is invariably in excess of that required by the usually-accepted equation $2R'_2SO_4 + C = 2SO_2 + CO_2 + 2R'_2O$. The course of the reaction was investigated by heating equal weights of sodium sulphate and silica with various proportions of wood charcoal in sealed Hessian crucibles, and collecting the evolved gases. It was found that the whole of the sulphur of the sulphate was expelled in the free state, and that the gases consisted of a mixture of carbonic anhydride and carbonic oxide. It would thus seem that the silica first decomposes the sodium sulphate, liberating sulphuric anhydride, which immediately splits up into sulphurous anhydride and oxygen, and that the carbon then decomposes the sulphurous anhydride, liberating sulphur, and forming the oxides of carbon. The final result may be represented by the equation $3Na_2SO_4 + 6SiO_2 + 5C = 3S + 4CO_2 + CO + 3(Na_2O,2SiO_2)$. Jn. W.

Lithium Nitride. By L. Ouvrard (*Compt. rend.*, **114**, 120—121).—When commercial lithium, containing 4·5 per cent. of nitrogen, together with silica and other impurities, is heated in an iron boat in a current of nitrogen, no noteworthy absorption takes place until a dull-red heat is reached; but at this temperature the metal becomes incandescent and swells up, forming a mass which is black and

spongy when cold, and appears to consist mainly of *trilithium nitride*, Li_3N. This substance reacts with water to form ammonia, scarcely any hydrogen being evolved, and, when heated in hydrogen, is completely decomposed into ammonia and metallic lithium. Jn. W.

Direct Combination of Nitrogen with Alkaline-earth Metals. By Maquenne (*Compt. rend.*, **114**, 25—26).—Amalgams containing 15 to 20 per cent. of barium, strontium, and calcium were prepared by electrolysing strong solutions of the chlorides, using mercury as the cathode, and, in the case of calcium, concentrating the product by distillation. When these amalgams are heated in an iron or metallic dish in a current of pure and dry nitrogen at a dull-red heat for half an hour until most of the mercury is expelled, and then for a few minutes at bright redness, nitrides of the alkaline-earth metals are obtained as brown products with a semi-metallic appearance. The barium compound, which is obtained the most readily of the three, sometimes forms yellowish, acicular crystals. The nitrides alter rapidly in moist air, and are decomposed by water with evolution of hydrogen and development of heat, ammonia and the hydroxide of the metal remaining in the liquid. The nitrides seem to be somewhat volatile.

The rapid combination between nitrogen and the metals of the alkaline-earths in complete absence of carbon or its compounds indicates the existence of considerable chemical attraction between them. C. H. B.

Magnesium Lead Bromide. By R. Otto and D. Drewes (*Arch. Pharm.*, **229**, 585—588).—A magnesium lead bromide,

$$PbBr_2,2MgBr_2,16H_2O,$$

similar to the double chloride and iodide (Abstr., 1891, 151, 984) is formed by dissolving lead bromide in a boiling concentrated solution of magnesium bromide, and may be obtained in crystals by allowing the solution to evaporate. It forms large, semi-transparent crystals, belonging probably to the monoclinic system; their hygroscopic nature, however, prevented a complete crystallographic examination. In water or in alcohol, the salt separates into its components.

With hydrogen sulphide, it behaves like the double iodide, and the lead is converted into sulphide; the double chloride does not so react.

The double bromide dissolves readily in dilute acetic acid. The water of combination separates at 140°. J. W. L.

Action of Ammonia on Cadmium Chloride. By W. Kwasnik (*Arch. Pharm.*, **229**, 569—572).—The action of ammonia on cadmium chloride in alcoholic solution is exactly similar to that of ammonia on zinc chloride (Abstr., 1891, 1157).

Anhydrous cadmium chloride was dissolved in ammonia; after filtering from the basic chloride, ammonia gas was passed into the solution until no longer absorbed, and the precipitate collected and dried at 50°. This salt, *ammoniocadmium chloride*, $Cd(NH_3Cl)_2$, is a white, crystalline powder, insoluble in ammonia, and resembles the zinc salt very closely.

When heated in a glass retort, ammonia is liberated, after which the residue melts, boils, and the distillate is obtained as a transparent, yellowish, glassy mass, which differs from the corresponding zinc salt only in its being less hygroscopic: its formula is

$$CdCl{\cdot}NH_3Cl.$$

It requires considerably less heat for its distillation than the zinc salt.

J. W. L.

Behaviour of Hydrogen towards Lead and other Metals. By G. Neumann and F. Streintz (*Monatsh.*, **12**, 642—660).—The authors have previously suggested (*Ann. Phys. Chem.* [2], **41**, 106, *et seq.*) that certain physical phenomena which occur at the negative plate of a secondary battery may be explained by the assumption that lead is capable of absorbing hydrogen. Attempts to prove that such is the case, under conditions which obtain in a secondary battery, have given no satisfactory results. When, however, hydrogen was passed over molten lead, the metal occluded only a small quantity, from 0·11 to 0·15 its volume, of the gas. Comparative experiments with other metals, in varying mechanical condition, showed their power of occlusion to be as follows:—Palladium, 502·35 times its volume; platinum, 6·48—49·30 times its volume; gold, 37·31—46·32 times its volume; copper, 4·78—4·81 times its volume; aluminium, 2·72 times its volume; iron, 9·38—19·17 times its volume; nickel, 16·85—17·57 times its volume; and cobalt, 59·31—153·00 times its volume. Silver does not appear to have the power to occlude hydrogen.

G. T. M.

Lead Chromate. By Lachaud and Lepierre (*Bull. Soc. Chim.* [3], **6**, 230—232).—A solution of lead chromate in warm binormal potassium hydroxide solution deposits, on cooling, orange-yellow, prismatic needles or silky tufts of basic lead chromate, $PbCrO_4,PbO$, which differ only in colour from those obtained by the fusion of lead chromate with potassium nitrate.

When lead chromate is boiled for a few minutes with strong potassium hydroxide solution (45 per cent.), dull, greyish-green scales of lead oxide are formed, of sp. gr. 9·51, and a basic chromate is often formed. Lead chromate, on fusion with potassium hydroxide, yields lead dioxide. An attempt to produce lead dichromate, by boiling together amorphous lead chromate (5 grams) with chromic anhydride (20 grams) and water (70 grams), was unsuccessful, but after a few minutes the whole of the lead salt becomes crystalline. Dark-red, orthorhombic crystals of melanochroïte, $2PbCrO_4,PbO$, of sp. gr. 5·81, are obtained when amorphous lead chromate (10—20 grams) is projected in small portions into a crucible containing fused sodium chloride (200 grams), and the contents maintained at a red heat for two hours; at the same time, orange crystals, of a compound $Pb_4Cr_5O_{16}$, resulting from the decomposition of lead chromate, are formed.

T. G. N.

Thallium Chromate. By Lachaud and Lepierre (*Bull. Soc. Chim.* [3], **6**, 232—235).—Thallium chromate is precipitated by potassium chromate from thallium sulphate solution as an amorphous,

lemon-yellow substance. A litre of boiling binormal potassium hydroxide solution dissolves 3·5 grams of thallium chromate, and, on cooling, deposits microscopic, six-faced prisms, ending in hexagonal pyramids. No basic chromate is formed, differing thus from the corresponding lead salt. Concentrated hot potassium hydroxide solution (31 per cent.) dissolves thallium chromate (18 grams per litre), which is almost entirely deposited as such on cooling. Similarly to the case of lead chromate, fused potassium hydroxide determines the formation of thallium sesquioxide, Tl_2O_3, from thallium chromate; the method of operation is as follows:—Thallium chromate (1 part) is projected into fused potassium hydroxide (10 parts); the liquid is at first yellow, but after fusion for two hours becomes cloudy, and crystals float therein; these are allowed to subside, and after decantation of the supernatant fused hydroxide containing the dissolved chromium sesquioxide, the crystals are again fused with potassium hydroxide, from which they are subsequently separated by washing, any traces of thallium chromate being removed by treatment with hot potassium hydroxide. Thus prepared, thallium sesquioxide is absolutely pure, and forms black, hexagonal plates, of sp. gr. 5·56 at 0°; it is insoluble in fused potassium hydroxide, but dissolves in hydrochloric acid to form thallic chloride, and is soluble with difficulty in sulphuric acid. The authors reserve to themselves the redetermination of the atomic weight of thallium by means of this compound. Thallium chromate is not altered by fusion with potassium nitrate, but recrystallises therefrom in right hexagonal prisms. A double salt, Tl_2CrO_4,K_2CrO_4, results from the fusion of thallium chromate and potassium chromate with potassium nitrate, but no double salt of lead and thallium chromates exists. Thallium chlorochromate is formed by the interaction of thallium chloride (1 part) and chromic anhydride (20 parts) in a small quantity of water; the small, prismatic crystals thus obtained are washed with chromic acid solution and dried in a vacuum on porous tiles; water decomposes this compound with formation of thallous chloride and chromic acid.

T. G. N.

Action of Carbonic Oxide on Iron and Manganese. By Guntz (*Compt. rend.*, **114**, 115—117).—With the view of clearing up the discrepancies between the statements of various writers on this subject, the experiments were repeated with pure metals prepared in a finely-divided state by heating their amalgams in a vacuum.

Iron appears to absorb carbonic oxide at a dull-red heat, carbon being set free, and a small quantity of carbonic anhydride formed. With manganese, the action is simpler, the products being practically only manganous oxide and carbon, no carbonic anhydride being formed. The reaction starts at 400°, and proceeds with such vigour as to render the mass incandescent, and cause a partial vacuum in the apparatus. The absence of carbonic anhydride confirms Moissan's view, that manganous oxide, unlike ferrous oxide, is not reducible by carbonic oxide. This view is also confirmed by the readiness with which manganese burns in carbonic anhydride and by the identity of the products with those which are formed when it is burnt in the monoxide. In the case of iron, the formation of carbonic anhydride,

and also that of ferrous oxide, as observed by Schützenberger, may be explained by means of the known reducibility of ferrous oxide by carbonic oxide, if it is assumed that the action of the metal itself on the monoxide resembles that of manganese. The monoxide is thus first reduced to carbon, and the ferrous oxide formed is then reduced to iron by a further quantity of the gas.

At very high temperatures, it is to be observed, the reactions of carbonic oxide with the metals are reversed, the metallic oxides being easily reducible by carbon, with the formation of carbonic oxide.

The above results furnish an explanation of the action of the blast furnace. The spongy iron reduced by the hydrogen and hydrocarbons in the upper part of the furnace meets carbonic oxide at a comparatively low temperature, and decomposes it, forming ferrous oxide and carbon. As this mass sinks, it enters a region of which the temperature is higher, although still below that at which ferrous oxide is reduced by carbon, and here the oxide meets with more carbonic oxide, and is reduced to the metal, the monoxide being oxidised to carbonic anhydride. Finally, in the lowest and hottest part of the furnace, the carbon which was reduced in the upper part, and with which the iron has remained in contact throughout its descent, unites with the metal to form a fusible carbide. Jn. W.

Hydrated Potassium Manganites. By G. Rousseau (*Compt. rend.*, **114**, 72—74).—When potassium manganate is heated at about 600° with potassium carbonate and chloride, it yields black lamellæ of the composition $K_2O,16MnO_2,6H_2O$. At a somewhat higher temperature, large, black lamellæ of the manganite, $K_2O,8MnO_2,3H_2O$, are formed. In an earlier paper (Abstr., 1887, 892—893), the formula $K_2O,7MnO_2$ was erroneously attributed to this compound, the analysis having been made on material dried at 150—160°. At the highest temperature obtainable with a Bunsen flame, the hydrate, $K_2O,16MnO_2,6H_2O$, is again formed, the changes being periodic, as in the case of sodium, barium, and strontium manganites. The proportions of potassium carbonate and chloride used have no influence on the result, and with the chloride alone the product

$$K_2O,16MnO_2,10H_2O$$

is obtained.

At an orange-red heat the crystals formed have the composition $K_2O,32MnO_2,10H_2O$.

If the materials are heated out of contact with the flame gases, for example, in a platinum dish in a tube through which a current of water vapour is passed, the same three hydrates are at first formed, but the alkali gradually volatilises. When the whole of the manganate has been decomposed, the anhydrous manganite is left, but the latter dissociates into free alkali and manganese dioxide. If the heating is continued, the dioxide gradually becomes completely converted into trimanganic tetroxide. Similar results are obtained in a vacuum at about 1000°. C. H. B.

The Variations in Colour of Cobalt Chloride. By Engel (*Bull. Soc. Chim.* [3], **6**, 239—251).—Although several hydrated

cobalt chlorides are described, only the following appear to be stable:—$CoCl_2 + H_2O$ (dark violet), $CoCl_2 + 2H_2O$ (violet-rose), and $CoCl_2 + 6H_2O$ (dark red).

Some observers ascribe the blue colour assumed by solutions of cobalt chloride, under definite conditions, to the formation of the anhydrous salt, although anhydrous cobalt chloride is bright blue in colour, and its solutions vary from a deep- to an indigo-blue. Hydrochloric acid of molecular constitution $HCl,6{\cdot}5H_2O$ dissolves cobalt chloride to form a blue solution. Cobalt chloride, in combining with 6 mols. of water, develops 21·9 Cal., or 3·5 Cal. per water molecule, whereas hydrochloric acid, having the molecular constitution $HCl,2H_2O$, in combining with 4·5 mols. of water, develops but 4·9 Cal., or only 1·1 Cal. per water molecule, from which thermochemical considerations simple dehydration appears infeasible. The rose-coloured hydrate, $CoCl_2 + 2H_2O$, remains unaltered in a stream of dry hydrogen chloride, but traces of water cause it to turn blue, and this behaviour points to the formation of a hydrochloride of cobalt chloride; this is supported by the fact that the solubility of cobalt chloride in water containing hydrochloric acid varies directly with the amount of hydrogen chloride present; and a saturated solution of cobalt chloride in hydrochloric acid contains less water than would be necessary to hold in solution the separate constituents, whilst if this solution be cooled to −23°, long, blue crystals, having the probable formula $CoCl_2,HCl + 3H_2O$, separate. The stability of this hydrochloride is dependent on the presence of excess of hydrogen chloride, for if zinc chloride be added to the blue solution, it becomes rose-coloured, whereas addition of calcium or lithium chlorides, which form compounds with hydrogen chloride without abstracting water, only determine a blue coloration, since anhydrous lithium or calcium chlorides develop less heat than does anhydrous cobalt chloride, and a blue compound, $CoCl_2,LiCl + 3H_2O$, corresponding with the author's hydrochloride, has been prepared by Chassevent. Wyrouboff has shown that when a saturated solution of cobalt chloride is heated to 100°, it becomes dark-blue, the violet salt, $CoCl_2 + H_2O$, being simultaneously formed; the author explains this as due to the superposition of the colours of the violet hydrate and of the blue hydrochloride of cobalt chloride, and the presence of the latter is dependent on the decomposition of cobalt chloride on heating, since the vapours of the boiling solution contain free hydrogen chloride. Again, the addition of zinc or mercuric chloride to a cobalt chloride solution at 100° determines a violet coloration, which is due to the hydrate $CoCl_2 + H_2O$. The blue coloration produced by alcohol is not a dehydration phenomenon, but is due to the formation of the alcoholic compound indicated by Potilitzin. The latter thinks that the change of colour of paper moistened with cobalt chloride solutions, when exposed to dry air, is due to capillarity, and to this the author offers objections, believing it to be due to the formation of a compound with cellulose, similar to those which this substance yields with the chlorides of aluminium, iron, zinc, copper, and tin, as described by Girard. T. G. N.

The Hydrates of Cobalt Chloride and their Alterations in Colour. By A. Potilitzin (*Bull. Soc. Chim.* [3], **6**, 264—266).—In addition to the hydrate $CoCl_2 + 6H_2O$, two other hydrates, $CoCl_2 + 2H_2O$ (violet-rose) and $CoCl_2 + H_2O$ (deep violet), exist. The former compound is formed at 45—50° or at the ordinary temperature over sulphuric acid, whilst the monohydrated salt is formed when this is heated at 100°, or is deposited as well-formed crystals when a solution of the dihydrate in absolute alcohol is heated to 95°. The alteration in colour of the red crystals of $CoCl_2 + 6H_2O$ is followed by their melting in their water of crystallisation. A perfectly dry crystal of the hexahydrate on being heated, effloresces, without change of colour until it melts at 54°, when it becomes more and more blue. These observations, together with the fact that during this change the hexahydrate loses in weight, point to its dissociation, resulting in the elimination of water and the formation of lower hydrates. $CoCl_2 + H_2O$ dissociates at 90—95°, but at a much lower temperature in aqueous solution, and the temperature at which the corresponding alteration in colour occurs is further lowered by the presence of dehydrating substances, whilst the more dilute the aqueous solution the higher becomes the temperature of dissociation. Hygroscopic substances, such as filter paper and porous inorganic materials, effect the same change. In no case does dissociation proceed further than to determine the formation of the monohydrated salt (compare Étard, this vol., p. 278). T. G. N.

Action of Heat on Solutions of Chromium Salts. By W. N. Hartley (*Chem. News*, **65**, 15—16).—In 1875, the author stated (*Proc. Roy. Soc.*, **33**, 372) that the action of heat on the violet hydrated compounds of chromium is not simply a dissociation of water molecules or of acid from base, but a true decomposition, resulting in the production of a different class of salts with different generic properties.

The thermochemical investigations of Recoura on the action of heat on solutions of chromic oxide (Abstr., 1891, 1430) fully confirm the author's views. L. de K.

Isomorphous Thorium and Uranous Sulphates. By W. F. Hillebrand and W. H. Melville (*Amer. Chem. J.*, **14**, 1—9).—When the oxide U_3O_8 is heated with dilute sulphuric acid (1 part of acid to 5 or 6 of water by volume) in a sealed tube at about 170°, green crystals of uranium sulphate, $U(SO_4)_2 + 4H_2O$, are formed. If uraninite, or mixtures in varying proportions of the oxides U_3O_8 and ThO_2, are decomposed in a similar manner, a green double sulphate of uranium and thorium is obtained, $(U,Th)(SO_4)_2 + 4H_2O$; the percentage of UO_2 and ThO_2 in these crystals varies with the proportions of the oxides in the original mixture; in the actual analyses the limits of the variation are UO_2 49·18, ThO_2 3·59 to UO_2 16·92, ThO_2 36·07 per cent. The thorium dioxide replaces the uranium dioxide isomorphously; the uranium sulphate crystallises in the rhombic system ($a : b : c = 1 : 1·9478 : 2·5755$); the double sulphate of uranium and thorium also crystallises in this system, and has nearly the same

axial ratio ($a : b : c = 1 : 1{\cdot}9194 : 2{\cdot}5563$); its habit, however, is tetragonal. C. F. B.

Alloy of Tin and Sodium. By H. Bailey (*Chem. News*, **65**, 18).—The author was struck by the uniformity in appearance and behaviour of several alloys of tin and sodium which had been prepared by heating a mixture of tin with excess of sodium in a crucible provided with a luted lid, through which a small hole had been drilled so as to allow the excess of sodium to escape as vapour. After cooling in an inert atmosphere, the contents of the crucible were examined and found to consist of a brittle mass externally covered with a slight white scoria, which, on fracture, revealed brilliant, crystalline facets of a beautiful bronze colour, quickly becoming tarnished with a grey powder.

An analysis of the compound gave percentages corresponding exactly with the formula Na_2Sn. The alloy is very suitable for the preparation of hydrogen, being readily decomposed by water.

L. de. K.

Palladious Oxide. By T. Wilm (*Ber.*, **25**, 220—224).—Palladium sponge, prepared by heating the compound $PdCl_2,2NH_3$, first in the air and then in a stream of hydrogen, is very similar in appearance to platinum sponge, except that it has a more silvery lustre. When it is heated in an open porcelain crucible with an ordinary burner, it rapidly darkens and turns a variety of colours, but on further heating it gradually assumes a dark, dirty, bluish-green hue, and then consists of a mixture of palladium and palladious oxide. When palladium sponge is heated in a stream of dry oxygen until its weight is constant, it is completely converted into palladious oxide, PdO; this compound is a dark, bluish-green powder, insoluble in acids, even in boiling aqua regia; it is readily reduced by hydrogen even at comparatively low temperatures, and it decomposes into oxygen and palladium when strongly heated. F. S. K.

Mineralogical Chemistry.

Theories of the Structure of Crystals. By A. Schönflies (*Zeit. physikal. Chem.*, **9**, 158—170).—In his work *Krystallsysteme und Krystallstruktur* (Leipzig, 1891), the author has discussed the classification of crystals according to symmetry and the theory of their structure chiefly from the geometrical standpoint. The present paper contains some explanatory observations bearing on the physical side of the question.

A uniform subdivision of the ordinary systems is proposed, namely, holohedral forms, enantiomorphous, hemimorphous, and paramorphous hemihedral, and tetartohedral forms. Thus the tetragonal system would be subdivided as follows:—

Holohedry.

Enantiomorphous (trapezohedral) hemihedry.

Hemimorphous hemihedry (hemimorphism).
Paramorphous (pyramidal) hemihedry.
Tetartohedry (hemimorphous tetartohedry).
Hemihedry with axis of the second species (sphenoidal hemihedry).
Tetartohedry with axis of the second species (sphenoidal tetartohedry). J. W.

So-called Amber of Cedar Lake, Canada. By B. J. Harrington (*Amer. J. Sci.*, **24**, 332—335).—The occurrence of mineral resins, resembling amber, in some of the coals and lignites of Canada has been known for many years. In 1890, on the west shore of Cedar Lake, near the mouth of the North Saskatchewan, a mineral of this character was found in large quantity, mixed with sand and fragments of partly decayed wood. It had evidently been washed up on the shore by the waves. On analysis, this so-called amber yielded :—

C.	H.	O.	Ash.	Total.
79·96	10·46	9·49	0·09	100·00

Although resembling amber in some of its characters, it may be classed provisionally as *retinite*, on account of its differing from amber in its behavionr with acids, its not yielding crystals of succinic acid on distillation, and its somewhat different ultimate composition. Although the origin of this resin is not known with certainty, there can be no doubt that it was derived from one of the tertiary or cretaceous lignites occurring on the Saskatchewan.

B. H. B.

Tourmaline from Siberia. By R. Prendel (*Zeit. Kryst. Min.*, **20**, 93).—A specimen of red tourmaline (sp. gr. 3·116) from the Urulga, in Siberia, gave on analysis the following results :—

SiO_2.	TiO_2.	F.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
38·36	0·13	0·56	9·54	40·10	0·24	0·58	4·06	1·69

MgO.	Li_2O.	K_2O.	Na_2O.	H_2O.	P_2O_5.
0·48	0·45	2·20	0·24	2·94	0·56

The formula is, therefore,

$$12SiO_2,8Al_2O_3,3B_2O_3,2(FeO,MnO),Na_2O(K_2O,Li_2O),3H_2O.$$

B. H. B.

Action of Water on Mica. By A. Johnstone (*Quart. J. Geol. Soc.*, **45**, 363—368).—In this paper the author gives details of the observations noted, and results of experiments carried out in an investigation into the nature of the changes produced by pure distilled water, and also by water saturated with carbonic anhydride, on the principal members of the mica family. He classifies the micas into two great classes, anhydrous and hydrated micas. The anhydrous micas include muscovite and biotite, and never contain more than 2·5 per cent. of water. The passage micas contain from 2·5 to 4 per cent. of water, and have intermediate physical characters. The hydrous micas contain at least 4 per cent. of water, and include

hydromuscovite and hydrobiotite. Under muscovite are included the varieties, potash or ordinary muscovite, soda muscovite, lepidolite, zinnwaldite, cryophyllite, and fuchsite. Under biotite are included rubellane, anomite, phlogopite, aspidolite, lepidomelane, and astrophyllite. Under hydromuscovite are included margarodite, euphyllite, paragonite, oellacherite, gilbertite, damourite, sericite, pregrattite, and cossaïte. Lastly, under hydrobiotite are included voigtite, vermiculite, jeffreysite, and pyrosclerite. The specimens of the anhydrous micas were exposed to the action of water, pure and carbonated, for a year, and at the end of that period it was found that all the chemical change effected was hydration, and that the hydrating process went on as readily in the pure water as in the aqueous solution of carbonic anhydride. The author noted that whenever anhydrous micas become hydrated, they always, at the same time, increase in bulk. B. H. B.

Hot Mineral Spring at Finca Huracatao, Salta, Argentine Republic. By F. Canzoneri (*Gazzetta*, **21**, ii, 462—465).—This water issues at a temperature of about 40° and has a sp. gr. of 1·0009 at 25°. It is colourless and transparent, and gives no deposit; it has a slight saline taste and a faint odour of hydrogen sulphide. It contains 0·035 gram per litre of free carbonic anhydride and 0·0036 gram of free hydrogen sulphide. The total weight of carbonic anhydride per litre is 0·082 gram. The residue from a litre, when dried at 100°, weighs 1·981 grams.

1 litre of the water contains, in grams:—

SiO_2.	Cl.	SO_3.	Na_2O.	K_2O.
0·050	1·050	0·025	0·487	0·073

CaO.	MgO.	Al_2O_3 and Fe_2O_3.
0·257	0·005	0·004

W. J. P.

Organic Chemistry.

Exchange of Chlorine, Bromine, and Iodine between Inorganic and Organic Haloïd Compounds. By M. Wildermann (*Zeit. physikal. Chem.*, **9**, 12—25).—The action of the iodides of copper, silver, mercury, tin, lead, arsenic, and antimony on the bromides of isobutylene, isoamylene, trimethylene, propylene, and ethylene was investigated, more particularly by determining, with standard sodium thiosulphate solution, the amount of iodine liberated in each reaction. The results obtained led the author to include other bromides in his investigations, and thus to the general result that the separation of iodine takes place not only in the case of isobutylene and isoamylene, which form no additive compounds with iodine, but with the halogen derivatives of the paraffins generally of the compo-

sition $C_nH_{2n}X_2$, $C_nH_{2n-1}X_3$, $C_nH_{2n-2}X_4$. Even in the case of the monohalogen derivatives, $C_nH_{2n+1}X$, decomposition takes place in perceptible amount. Generally, therefore, the interaction of inorganic and organic haloïd compounds is reciprocal. Comparing the action on trimethylene bromide with that on other compounds of the composition $C_nH_{2n}Br_2$, it appears that two iodine atoms which are united with neighbouring carbon atoms more readily combine with and are eliminated from the hydrocarbon molecule than when attached to non-neighbouring carbon atoms. The influence of the organic radicle on the velocity of the reaction is very marked, the velocity being, at any moment, proportional to the amounts of unchanged bromide and iodide still present. The separation of iodine in the free state by the action of certain metallic iodides on bromides of the composition $C_nH_{2n}Br_2$, $C_nH_{2n-1}Br_3$, and $C_nH_{2n-2}Br_4$ is apparently general when the bromine atoms are united to neighbouring carbon atoms, unsaturated hydrocarbons or their halogen derivatives being at the same time formed. It forms, therefore, a general method for preparing unsaturated hydrocarbons from their bromides. H. C.

Nitration of Hydrocarbons of the Methane Series. By Konovaloff (*Compt. rend.*, **114**, 26—28).—When normal hexane is heated in sealed tubes at 130—140° with nitric acid of sp. gr. 1·075, it yields 50 per cent. of the theoretical quantity of crude nitrohexane, which, when fractionated, yields 30 per cent. of the theoretical quantity boiling at 175—177°. The greater part distils at 176°; sp. gr. at 0° = 0·9509, or at 20° compared with water at 0° = 0·9357. The nitrohexane dissolves in boiling, concentrated, aqueous potash, and with development of heat in alcoholic potash. With nitrous acid, its solutions give a blue-green coloration, indicating the formation of a pseudo-nitrol, but it yields no nitrolic acid. When reduced with zinc and acetic acid, it yields methyl butyl ketone and secondary hexylamine. It follows that the nitrohexane is a secondary derivative with the formula $NO_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me$.

Normal octane, under similar conditions, yields a secondary nitrooctane, which, when reduced, yields a ketone and an amine.

C. H. B.

Aliphatic Nitro-compounds. By V. Meyer (*Ber.*, **24**, 4243—4245).—A preliminary notice on experiments which are being carried out by the author and his pupils.

Iodomethylene, on treatment in ethereal solution with silver nitrate, gives an oil from which, on addition of sodium ethoxide, an explosive white *salt*, $NO_2{\cdot}CHINa$, is obtained. Iodallyl, when treated in the same way, yields a very explosive salt, $NO_2{\cdot}C_3H_4Na$; this, on acidification, gives *nitropropylene* as a light, mobile oil, volatile with ether vapour; whilst on treatment with diazobenzene sulphate, it furnishes a crystalline *azo*-derivative, $NO_2{\cdot}C_3H_4{\cdot}N_2{\cdot}Ph$. When boiled with silver nitrate, ethylene bromide yields an oil giving an explosive salt with sodium ethoxide. The investigation is proceeding.

A. R. L.

Action of Ammonia on Mercuric Cyanide and Haloïd Combinations of this Salt. By R. Varet (*Bull. Soc. Chim.* [3], **6**,

220—230).—In addition to the compounds which have been previously examined by him (compare Abstr., 1890, 351; 1891, 161, 655, 1441), the author describes the preparation of some simple additive compounds which ammonia yields with mercuric cyanide.

The salt $2HgCy_2,4NH_3,H_2O$ is obtained by treating a saturated ammoniacal solution of mercuric cyanide with gaseous ammonia and, after filtration, cooling the filtrate in a freezing mixture. It forms long, white, prismatic crystals, which lose ammonia and water on exposure to the air, and decompose at 100°, leaving a residue of mercuric cyanide.

The salt $2HgCy_2,2NH_3,H_2O$ separates at 0° in small, white, granular crystals from a saturated ammoniacal solution of mercuric cyanide to which ammonia gas (one-tenth part by weight) is added. It is an unstable substance, is very soluble in aqueous or alcoholic ammonia, and decomposes at 100°.

The compound $HgCy_2,2NH_3$ is deposited from a saturated alcoholic ammoniacal solution of mercuric cyanide after saturation with dry ammonia gas and subsequent cooling. It loses half its ammonia on exposure to air, and the whole on warming for a few hours at 100°.

The compound $HgCy_2,NH_3$ is produced by warming, in a stoppered bottle at 40°, a saturated ammoniacal solution of mercuric cyanide with excess of the salt. The filtered solution deposits the compound as small, hard, granular crystals, which are more stable than the preceding salts. It is soluble in water and in ammonia solution, and is resolved at 100° into its constituents.

The salt $HgCy_2,2NH_3$ is obtained as an amorphous, white substance by passing ammonia gas over dry mercuric cyanide at 100° for 30 hours. The compound evolves ammonia and absorbs water on exposure to the air, but the water may be again displaced by the action of a current of dry ammonia gas. T. G. N.

Polymerisation of Nitriles. By E. v. Meyer (*J. pr. Chem.* [2], **45**, 63—64; compare Abstr., 1889, 114, 577).—Hanriot and Bouveault (*Bull. Soc. Chim.*, **51**, 170; compare Abstr., 1889, 841) regard the evolution of ethane from ethyl cyanide and sodium as due to the presence of ether, and have overlooked the formation of sodium cyanide. So far from ether being essential to the production of the ethane, the reaction takes place in exactly the same way in benzene, ethane being evolved and sodium cyanide formed. Whether the sodium in the polymerisation product is united to the nitrogen or to the carbon is as uncertain as whether the sodium is attached to the carbon or oxygen in ethyl sodacetoacetate. A. G. B.

Thermal Value of the Hydroxyl Groups of Glycol. By De Forcrand (*Compt. rend.*, **114**, 123—126).—Monatomic primary alcohols, as a rule, give off a constant quantity of heat, +32 Cal., when sodium is substituted for the alcoholic hydrogen (all substances except hydrogen calculated as solid). The first hydroxyl group of glycol, however, gives more than this, namely, +39 Cal., whilst the second gives less, +27·7 Cal.

By assuming, however, that monosodium glycol forms a compound

with glycol similar to that which sodium methoxide forms with methyl alcohol, the apparent anomaly may be explained, for the heat evolved in the formation of the molecular compound will increase the amount evolved in the first stage, whilst that absorbed in its decomposition will diminish the amount evolved in the second stage. The values calculated in this way, due allowance being made for heat of fusion and solidification, agree satisfactorily with the normal value.

Jn. W.

A New Mode of Formation of Symmetrical Tribromhydrin. By A. Kronstein (*Ber.*, **24**, 4245—4247).—When equivalent quantities of trimethylene bromide and bromine are heated at 120° in a sealed tube for nine hours, and the product washed and thrice fractionated, symmetrical tribromhydrin is obtained as a colourless oil of sp. gr. 2·44 at 25°; it boils at 219—222°, and solidifies to a crystalline mass on cooling to 0°. If the bromination is conducted in the presence of iron wire (see next abstract) at 100°, the yield of tribromhydrin is almost quantitative. The tribromhydrin is likewise obtained in almost quantitative yield by brominating propylene bromide at 100° in the presence of iron wire; the same compound is produced by similarly treating propyl bromide and isopropyl bromide, employing bromine (2 mols.). Experiments are in progress on the preparation of higher symmetrical brominated derivatives of hydrocarbons, and the related polyhydric alcohols. A. R. L.

Substitution in the Aliphatic Series. By V. Meyer and F. Müller (*Ber.*, **24**, 4247—4250).—The production of symmetrical tribromhydrin (preceding abstract) is not in accordance with the rule that, by the introduction of a second halogen atom into a compound, the newly entering halogen atom attaches itself to that carbon atom which carries the other halogen atom. Linnemann has shown that compounds of the type of ethylene bromide are formed when ethyl bromide is brominated, but Tawildarow (*Annalen*, **176**, 12) obtained ethylene bromide together with ethylidene bromide by brominating ethyl bromide at 200°; whereas Städel (*Annalen*, **195**, 182) obtained ethylidene chloride exclusively by chlorinating ethyl chloride, and the production of ethylene bromide observed by Tawildarow has been generally regarded as due to secondary reactions taking place at the high temperature. The author finds that when ethyl bromide and bromine are heated together in molecular proportion with iron wire in a sealed tube at 100° for an hour, ethylene bromide is the sole product; similarly ethyl chloride and antimony pentachloride yield exclusively ethylene chloride. Propyl and isopropyl bromide are readily converted into propylene bromide, $CHMeBr{\cdot}CH_2Br$, and it is unnecessary to employ sealed tubes. Experiments are in progress on the bromination of the fatty acids by this method. A. R. L.

Production of Dextrin. By P. Petit (*Compt. rend.*, **114**, 76—78).—The author has heated starch at definite temperatures for different lengths of time with different proportions of nitric acid, and has determined the rotatory power and reducing power of the product.

Direct experiments showed that if the products were digested with water at 40—50° for half an hour, the whole of the glucose and dextrin was dissolved, whilst the starch could be filtered off, dried, and weighed. The rotatory power of the solution is the sum of the rotatory powers of the glucose and dextrin present. Fermentation with pure yeast, after addition of ammonium phosphate and potassium sulphate, destroys all the glucose, and the loss of rotatory power gives the proportion of glucose present.

The starch, previously moistened with 30 per cent. of water, was mixed with 0·2, 0·3, 0·5, 0·8, and 2·0 per cent. of nitric acid, dried at 50°, passed through a sieve, and heated at 125°. The following table shows the proportion of glucose (as determined by reducing power) per 100 parts of dextrin.

Percentage of nitric acid.	Time of heating.				Unaltered starch per 100 parts dextrin.
	1 hr.	2 hrs.	3 hrs.	4 hrs.	
0·2	3·9	5·06	3·6	2·8	0·003
0·3	7·2	5·3	3·6	3·0	0·002
0·5	7·3	6·07	4·2	3·1	0·001
0·8	8·06	6·3	4·5	4·0	traces
2·0	9·5	7·1	5·4	4·5	traces

With 0·8 and 2·0 per cent. of acid, the whole of the starch disappears after an hour's heating at 125°. For a given quantity of acid, the reducing power diminishes as the time of heating is prolonged. For a given time of heating, the reducing power increases with the quantity of acid. For a given quantity of acid, the diminution of reducing power is more rapid the higher the temperature.

The product contains a small quantity of some substance which reduces Fehling's solution, but is not fermentable. C. H. B.

Fixation of Iodine by Starch. By E. Rouvier (*Compt. rend.*, **114**, 128—129).—When iodine is added to a clear aqueous solution of starch in the presence of ammonium chloride, iodide of starch is precipitated, and may be collected. The amount of iodine needed to exactly precipitate the starch, as determined by the absence of the latter from the filtrate, is directly proportional to the amount of starch present, and the iodide thus formed is capable of taking up more iodine, the amount of which appears to be dependent on the quantity of ammonium chloride present. Jn. W.

Unsaturated Aliphatic Amines. By C. Paal (*Ber.*, **24**, 4253).—The author has recently, in conjunction with A. Heupel (this vol., p. 30), described dibromopropylcarbamide, but overlooked the previous description of this compound by Andreasch (Abstr., 1884, 732). The compound melts at 111·5°, which agrees practically with the value given by Andreasch, whereas the melting point (163°) recorded by the author and Heupel is incorrect. When an aqueous solution of the compound is evaporated, bromopropylenecarbamide hydrobromide is obtained which agrees in every respect with Andreasch's description.

Bromopropylenecarbamide probably belongs to the pentoxazoline class (Gabriel and Elfeldt, this vol., p. 212), a view which is favoured by the observation of Andreasch (*loc. cit.*), that the bromine atom is not displaced by treatment with tin and hydrochloric acid; the formation of the hydrobromide from dibromopropylcarbamide would therefore be represented thus :—

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH = CH_2<\begin{matrix}CHBr{\cdot}CH_2\\O-C(NH)\end{matrix}>NH,HBr.$$

A. R. L.

Nitroguanidine. By G. Pellizzari (*Gazzetta*, **21**, ii, 405—409).—Jousselin (Abstr., 1878, 132; 1879, 613, 914) obtained a substance which he termed nitrosoguanidine by dissolving guanidine nitrate in fuming nitric acid, treating with concentrated sulphuric acid, and precipitating by pouring into cold water. The author has prepared this compound, and finds that it is certainly not nitrosoguanidine, but most probably *nitroguanidine*, $NO_2{\cdot}N{:}C(NH_2)_2$. It crystallises from water in colourless needles which decompose at 225° with evolution of ammonia, and do not give the reactions for a nitrate or a nitrite. It dissolves in cold aqueous potash, and is precipitated unaltered by acids; on heating or allowing the solution to remain for some time, carbonic anhydride, ammonia, and nitrous oxide are liberated, 1 mol. of the compound yielding approximately 1 mol. of nitrous oxide. On reducing nitroguanidine in very dilute solution by warming with stannous chloride, ammonium chloride and guanidine hydrochloride are obtained, together with traces of a base which very readily reduces ammoniacal silver nitrate. This substance may be amidoguanidine. W. J. P.

Some Reactions of Trithioformaldehyde and Formaldehyde. By G. Pulvermacher (*Ber.*, **25**, 304—311).—With the object of preparing methylenediacetamide (diacetylmethylenediamine), the author boiled Baumann's trithioformaldehyde (m. p. 216°) with an aqueous solution of acetamide in a reflux apparatus, but after several hours no reaction had taken place; freshly precipitated mercuric oxide was then added to the mixture, and it was again boiled, the products being in this case mercuric sulphide, formaldehyde, and unaltered acetamide.

Methylenediacetamide (*diacetylmethylenediamine*), $CH_2(NHAc)_2$, is obtained as follows:—Dry mercury acetamide (3 mols.) is heated with somewhat more than the calculated quantity (1 mol.) of trithioformaldehyde in a bath of sulphuric acid; darkening commences at 150°, and an energetic reaction sets in at 195°, and the now black melt froths up with the evolution of vapour having the penetrating odour of formaldehyde, and burning with a violet flame; the volatile products (see below) are condensed in a ∪-tube, attached to the flask and surrounded by water. The contents of the flask are extracted repeatedly with boiling water, the aqueous solution evaporated, and the residue dissolved in boiling alcohol, the solution being treated with animal charcoal and filtered, when the compound separates in four-sided prisms; it melts at 196°, boils with partial carbonisation at

288° (uncorr.), is extremely soluble in water, fairly so in alcohol, sparingly in light petroleum, benzene, and chloroform, but insoluble in ether. When the compound is boiled with dilute hydrochloric acid or sodium hydroxide, it is decomposed into formaldehyde, ammonia, and acetic acid; its aqueous solution has a neutral reaction. The *aurochloride*, $CH_2(NHAc)_2,HAuCl_4$, separates in large, six-sided crystals, when the compound is added to a solution of auric chloride in hydrochloric acid; it is very readily soluble in water and alcohol. The liquid which condensed in the U-tube (see above) was found to consist of formaldehyde, water, and acetonitrile.

Methylenedithioacetamide, $CH_2(NH\cdot CSMe)_2$, is formed when methylenediacetamide (5 mols.) is boiled with phosphorus pentasulphide (2 mols.) on the water-bath for two hours; the benzene solution is decanted from resinous products, evaporated, and the crystalline residue boiled with carbon bisulphide to remove the admixed sulphur; it is then crystallised from boiling water, whereby almost the whole separates, on cooling, in yellowish-white, spear-shaped needles; it is odourless, is soluble in alcohol, ether, and chloroform, and sparingly so in benzene; it dissolves in cold alkalis and is precipitated unaltered by hydrochloric acid. The aqueous solution gives an amorphous, yellow precipitate with mercuric chloride which becomes black on heating; the sulphur is removed by mercuric oxide, with the formation of acetamide. When treated at the ordinary temperature with alcoholic hydrochloric acid, or if boiled with aqueous alkalis or acids, the compound decomposes into formaldehyde, acetic acid, ammonia, and hydrogen sulphide; whilst methyl iodide reacts on a solution in chloroform with the production of a solid substance insoluble in indifferent solvents, but decomposed by water, alcohol, and glacial acetic acid, a penetrating, mercaptan-like odour being evolved.

Methylenedibenzamide, $CH_2(NHBz)_2$, is formed by heating trithioformaldehyde with benzamide at 200°; it separates from alcohol in white needles, melts at 219°, and decomposes when heated with dilute hydrochloric acid into formaldehyde, ammonia, and benzoic acid.

When aqueous solutions of formaldehyde and acetamide are mixed, a few drops of hydrochloric acid added, the mixture repeatedly agitated, and after three days evaporated on the water-bath, a certain quantity of methylenediacetamide is obtained. Benzamide does not react with formaldehyde in the presence of hydrochloric acid in aqueous solution, but in alcoholic solution methylenedibenzamide is formed. A. R. L.

Crotonaldoxime and Allyl Cyanide. By T. Schindler (*Monatsh.*, **12**, 637—638; compare this vol., p. 32).—The author has previously shown (*loc. cit.*) that crotonaldoxime is converted into the nitrile of crotonic acid when heated with acetic anhydride. In order to determine whether the oxime has the α- or β-configuration, he has treated the crystalline substance with acetic anhydride in the cold (compare Hantzsch, Abstr., 1891, 443). The product consisted chiefly of the nitrile, which indicates that the oxime has the β-configuration; but, at the same time, a small quantity of a viscid, colourless, odourless oil was formed. G. T. M.

Water of Crystallisation. By T. Salzer (*Arch. Pharm.*, **229**, 629—631).—The author gives a complete list showing the proportion of water of crystallisation which occurs in the salts of formic and acetic acids (see also this vol., p. 140). Four salts of both acids crystallise without water, and copper formate crystallises with 2 mols. H_2O. The formates of barium, strontium, and calcium crystallise with more water than the corresponding acetates, and in all the other cases (10) the formates contain less water than the corresponding acetates. J. W. L.

Alkyl and Acidyl Sulphides. By S. H. Davies (*Ber.*, **24**, 4251).—In the description of the preparation of thioacetic anhydride (this vol., p. 300), acetic acid was erroneously printed for acetic anhydride. A. R. L.

Preparation of Methylpropylacetic Acid from Ethyl Acetoacetate and from Diethyl Malonate. Solubility of the Salts of Methylpropylacetic Acid and of Trimethylacetic Acid. By E. Stiassny (*Monatsh.*, **12**, 589, 601).—The author has obtained methylpropylacetic acid in small quantity by the hydrolysis of methyl methylpropylacetoacetate, COMe·CMePr·COOMe (b. p. 200—205°), which results from the methylation of ethyl sodiopropylacetoacetate, with excess of methyl iodide in methyl alcoholic solution. Methylpropylacetic acid is readily obtained in quantity from diethyl malonate by propylation, methylation, and subsequent hydrolysis of the resulting acid (compare Conrad and Bischoff, *Annalen*, **204**, 121). The best yield was obtained as follows:—Propyl iodide was mixed with diethyl malonate, and added little by little to sodium ethoxide. The resulting diethyl propylmalonate, $CHPr(COOEt)_2$, boiled at 219—222°, and on hydrolysis with potash gave propylmalonic acid. The methylation of the propyl derivative was induced in a similar way, and the resulting diethyl methylpropylmalonate boiled at 220—223°. The product was hydrolysed with potash, and converted into the calcium salt, which was purified by recrystallisation, decomposed with hydrochloric acid, and the liberated acid separated by shaking with ether. On evaporation of the ethereal solution, a white, crystalline mass of methylpropylmalonic acid, $CMePr(COOH)_2$, which crystallised well from benzene and melted at 106—107°, was obtained. The acid is very soluble in water, chloroform, and ether, and is readily converted into methylpropylacetic acid, when heated in an oil-bath until no more carbonic anhydride escapes.

Silver methylpropylacetate crystallises from water in gleaming, feathery flocks; the solubility is given by the formula $S = 0{\cdot}51166 + 0{\cdot}00172\,(t-1) + 0{\cdot}00001512\,(t-1)^2$; the *calcium salt* crystallises with 3 mols. H_2O (compare Lieben and Zeisel, *Monatsh.*, 1883; and Kelbe and Warth, (*Ber.*, **15**, 308), and has the solubility $S = 16{\cdot}4994 - 0{\cdot}08375\,(t-1) + 0{\cdot}0006424\,(t-1)^2$.

Silver trimethylacetate has a solubility given by the formula $S = 1{\cdot}1038 + 0{\cdot}005131\,(t-1) + 0{\cdot}00004642\,(t-1)^2$. G. T. M.

Derivatives of Daturic Acid. By E. Gérard (*J. Pharm.* [5], **25**, 8—13; compare Abstr., 1890, 1395).—Normal potassium daturate forms transparent, crystalline grains, soluble in a little boiling water; the solution forms a lather when shaken, and gives a precipitate with common salt. The addition of much water decomposes the salt, setting free the alkali, and retaining an acid salt in solution, which crystallises out in colourless, crystalline laminæ. The corresponding sodium salts are very similar. Copper daturate obtained from alcoholic solutions of the acid and copper acetate forms crystalline needles, which dry to a light granular powder of a bluish-green colour. This salt is anhydrous, insoluble in water and ether, scarcely soluble in cold 90° alcohol. Normal lead daturate is obtained as a heavy, white, amorphous powder, which is not moistened by water. The salt is insoluble in cold alcohol and dry ether, and only very slightly soluble in boiling alcohol or dry ether. It melts at 104—105° without decomposition. Silver daturate, $C_{17}H_{33}AgO_2$, obtained by precipitating an aqueous solution of the sodium salt by means of silver nitrate, forms a very voluminous, white precipitate, which, when moist and exposed to light, rapidly becomes dirty grey. When crystallised from alcohol and dried in a vacuum, it forms small, nacreous scales, which are scarcely affected by exposure to light. The salt is insoluble in water and ether, but soluble in aqueous ammonia.

Daturone, $C_{33}H_{66}O$, is obtained by distilling the acid over excess of slaked lime, when the oily distillate solidifies on cooling, and is purified by crystallisation from hot 90° alcohol. It forms beautiful spangles with a pearly lustre, and melts at 75·5—76°. It is insoluble in water and in cold 75° alcohol, soluble in boiling alcohol, and very soluble in ether, benzene, and chloroform.

Monobromodaturic acid, $C_{17}H_{33}BrO_2$, was obtained by heating daturic acid with bromine and water in a sealed tube at 134—140° for 18 hours. Neither this acid nor its sodium salt could be crystallised.

J. T.

New Acid of the $C_nH_{2n-4}O_2$ Series. By A. Arnaud (*Compt. rend.*, **114**, 79—81).—The seeds of a shrub belonging to the genus *Picramnia* or *Tarari*, widely distributed in Guatemala, contain 67 per cent. of a fatty compound easily soluble in carbon bisulphide. The crude substance melts at 47°, and crystallises readily from ether in large, nacreous crystals. When saponified, it yields 95 per cent. of an acid and a quantity of glycerol corresponding with a triglyceride. The crude acid melts at 49—50°, and by repeated crystallisation from alcohol of 90°, the melting point is raised to 50·5°. It has the composition $C_{18}H_{32}O_2$, and is monobasic; the potassium salt is only slightly soluble in cold alcohol, but crystallises well from hot alcohol; the silver salt is amorphous and insoluble.

When treated with bromine in presence of chloroform, it yields an additive product $C_{18}H_{32}Br_2O_2$, which forms a crystalline mass very soluble in chloroform, alcohol, and ether. The bromo-acid is monobasic, and the potassium salt crystallises in long, very deliquescent needles. The direct action of bromine on the solid acid yields a

tetrabromide, $C_{18}H_{32}Br_4O_2$, which separates from strong alcohol in small, brilliant, waxy crystals melting at 125°.

The author calls the new acid *tariric acid;* the fat of the tariri being a triglyceride of the formula $C_3H_5(C_{18}H_{31}O_2)_3$. C. H. B.

Ethyl Acetoacetate. By J. W. Brühl (*Ber.*, **25**, 366—370).—A reply to a recent paper by Nef (this vol., p. 140) on the constitution of this compound. The fact that on treatment with sodium in ethereal solution ethyl diethylacetoacetate is reduced, whilst ethyl acetoacetate is unchanged, does not prove that the one compound is a ketone, and the other an unsaturated alcohol; it merely shows that some ketones are less stable than others towards reducing agents. The action of sodium on ethyl acetoacetate is similar to its action on ethyl camphocarboxylate, the ketones becoming converted into the salts $ONa{\cdot}CMe{:}CH{\cdot}COOR$ and $C_8H_{14}<\begin{matrix}C{\cdot}COOR\\ \|\\ C{\cdot}ONa\end{matrix}$ respectively.

Ethyl malonate being insoluble in soda, whilst ethyl acetoacetate readily dissolves, proves that the sodium salt of the latter compound is more readily formed than that of the former; no conclusion can be drawn as to the presence or absence of a hydroxyl group, since phthalic, succinic, and cinnamic acids do not react with sodium in ethereal solution; the same applies to terpineol, whilst menthol and borneol react far less readily than either camphor or menthone, which are undoubtedly ketones.

The recent syntheses of ethylcamphor and of ethyl camphocarboxylate show Nef's assumption, that the sodium in carbonyl compounds is never directly linked to a carbon atom, to be erroneous; this is still more strikingly exhibited in the case of menthone, which combines with two atoms of sodium, and yields a dicarboxylic acid; Pechmann (this vol., p. 431) has arrived at similar conclusions from his study of the potassium salts of ethyl acetonedicarboxylate.

The author has recalculated his determination of the molecular refraction of ethyl acetoacetate, employing the expression $\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}$; the result proves, as before, that at ordinary temperatures, and in the free state, the compound is represented by the ketone formula.

J. B. T.

Nitro-derivative of Methyl α-Hydroxypropionate. By G. de Varda (*Gazzetta*, **21**, ii, 359—361).—The nitro-derivative of methyl α-hydroxypropionate, $NO_2{\cdot}O{\cdot}CHMe{\cdot}COOMe$, is prepared by dropping methyl α-hydroxypropionate into a mixture of 2 parts of sulphuric acid (sp. gr. 1·84) and 1 part of nitric acid (sp. gr. 1·4), the temperature being kept at 0° during the reaction. The pure product is a colourless liquid, with an ethereal odour and a sweetish but subsequently pungent taste. Its sp. gr. at 7° = 1·2488. It distils at 166—168° (uncorr.), dissolves in alcohol, ether, acetic acid, &c., but is insoluble in water. It is decomposed by hot hydrochloric or sulphuric acid; when ignited, it burns with an olive-coloured flame.

S. B. A. A.

Cotton-seed Products. By G. Papasogli (*L'Orosi*, **14**, 217—229).—Crude cotton-seed oil contains 65·2 per cent. of solid and 34·8 per cent. of liquid fats; the former consisting mainly of tripalmitin, which, after repeated crystallisation from absolute alcohol, melts at 46° and solidifies at 45° (Chittenden and Smith found the melting point of tripalmitin to be 62°). On saponifying the oil and decomposing the soap thus formed by means of a mineral acid, the product contains 60·24 per cent. of solid fatty acids, 30·36 per cent. of liquid fatty acids, and 9·4 per cent. of glycerol.

The solid portion consists almost entirely of palmitic acid, but on recrystallising it from benzene, a small quantity of a white fat of waxy appearance is left undissolved. The liquid portion, after separation of the small quantity of palmitic acid in solution, is converted into a barium salt, and this, on decomposing it with an aqueous solution of tartaric acid, leaves a straw-yellow acid oil, soluble in alcohol, benzene, and ether. This has the composition $C_{20}H_{36}O_3$ ($C_{20}H_{38}O_3$?), and is termed by the author *cotonoleïc* acid. It has an acid reaction, and becomes very thick at −17°, but without solidifying. It deepens in colour on exposure to the air, acquiring a reddish tint, and gradually thickening; when exposed to an atmosphere of oxygen, the latter is rapidly absorbed. The *potassium* salt is very freely soluble in alcohol and water; the *silver* salt, $C_{20}H_{37}O_3Ag$, is yellowish-white, insoluble in water, and unaffected by light; when dry, it acquires a pale-maroon colour; it decomposes at 110—140°. The *barium* salt, $(C_{20}H_{37}O_3)_2Ba$, is white and soft when freshly prepared, but rapidly hardens and becomes brittle.

Besides the combinations of glycerol with palmitic and cotonoleïc acids, there exists in cotton-seed oil a compound isomeric with paraldehyde, $(C_2H_4O)_3$. This is best isolated by saponifying the oil with baryta-water, separating the insoluble barium soaps, precipitating the barium in solution by sulphuric acid, extracting the clear liquid with ether, and evaporating the extract. The residue is of a syrupy consistency, and of the same colour as the oil; it dissolves readily in alcohol and water, the aqueous solution having an acid reaction and reducing Fehling's solution; it readily combines with alkalis, forming compounds which have a resinous appearance when dry. The *lead* compound is a brownish-red, vitreous substance; the *silver* derivative, $C_6H_{11}O_3Ag$, is white when freshly precipitated, but rapidly turns black, even in the dark.

The author has found that the alcohol employed in Bechi's method for the detection of cotton-seed oil in olive oil is occasionally able to reduce silver nitrate on warming, especially if pure colza oil is added to it; such alcohol may be purified by distilling over potash or lime, and rejecting the first portions of the distillate, but a blank experiment is always necessary as a check. S. B. A. A.

Dehydracetic Acid. By F. Feist (*Ber.*, **25**, 315—335; compare following abstracts).—Bromodehydracetic acid, $C_8H_7BrO_4$, is prepared according to Perkin's method, by the action of bromine (35 grams) on dehydracetic acid (5 grams) dissolved in chloroform (50 grams); the

yield is 81—82 per cent. of the theoretical; the acid may be purified either by sublimation or by recrystallisation from methyl alcohol.

Oxydehydracetic acid, $C_8H_8O_5$, is obtained by treating the bromo-compound with mercuric cyanide, or with alcoholic potash; in the latter case, the finely divided acid is intimately mixed with two parts of powdered potassium hydroxide and a little absolute alcohol, and allowed to remain for 5—8 days; the yield is 75 per cent. of the theoretical. The electrolytic conductivity of the acid is $k = 0{\cdot}159$, $\mu\infty = 360$; it appears to contain only one carboxyl group, together with a replaceable hydrogen atom, since on titration one equivalent of soda is required with methyl-orange as indicator, but when phenolphthaleïn is employed nearly two equivalents of alkali are neutralised; the molecular weight of the acid, determined by Raoult's method, is 195·5. It yields oxalic acid on oxidation with alkaline permanganate, and on heating with water at 120° complete decomposition ensues.

The *sodium salt*, $C_8H_7O_5Na + H_2O$, is crystalline, the increase in the conductivity $\Delta = 10{\cdot}9$ from $v_{32} - v_{1024}$ shows it to be a normal salt. The *barium salt*, $C_8H_6O_5Ba + 5H_2O$, is also crystalline. With orthotoluylenediamine, the corresponding salt $C_8H_8O_5,C_6H_3Me(NH_2)_2$ is formed; this is sparingly soluble, and melts at 147° with decomposition. The *ammonium salt* melts at 178°. Phenylhydrazine reacts with the oxy-acid; the product is pale-yellow, melts at 185° with decomposition, and is readily soluble in alcohol, ether, or alkalis; it has the formula $C_{20}H_{18}N_4O_3$, and cannot be recrystallised.

On fusing the oxy-acid with ammonium acetate, a compound is obtained crystallising from alcohol in needles which melt at about 20°, and giving a deep-blue coloration with ferric chloride; the yield is very small. Three compounds, $C_{12}H_{12}O_8$, $C_{10}H_{10}O_7$, and $C_{10}H_8O_6$, are obtained by heating oxydehydracetic acid with concentrated hydrochloric acid in a sealed tube for several hours at 50—56°. The first of these, $C_{12}H_{12}O_8$, is a yellow, crystalline powder soluble in alcohol; it melts at 246° with decomposition, and gives an intense, deep-violet coloration with ferric chloride; determinations of the molecular weight agree with the above formula, and the electrical conductivity proves the compound to be a bibasic carboxylic acid; it is obtained in small quantity as a bye-product in the preparation of hydroxydehydracetic acid, and also by the action of sodium in alcoholic solution on bromodehydracetic acid. The *barium salt* is a pale, rose-coloured, crystalline powder; the *sodium salt* is yellow in solution; the *ammonium salt* is colourless, and melts at 185°. No definite compounds could be isolated by the action of orthotoluylenediamine, phenylhydrazine acetate, or soda on the acid. On heating the ammonium salt with 60 parts of concentrated alcoholic ammonia in a sealed tube for several hours at 100°, a compound is obtained crystallising from alcohol in colourless, lustrous plates which melt at 280—285°, give a violet coloration with ferric chloride, and a red coloration with isatin and sulphuric acid; it has the formula $C_{24}H_{27}N_3O_{13}$, and appears to be formed by the substitution of three oxygen atoms by three imido-groups in 2 mols. of the preceding acid; it is insoluble in hydrochloric acid, but dissolves in soda, and the vapour imparts a carmine-red coloration to a pine-shaving

moistened with hydrochloric acid. The substance sublimes with partial decomposition when cautiously heated, and yields a product which crystallises in colourless, lustrous plates, melts at 250°, and yields a blue coloration with ferric chloride. On heating the above ammonium salt (m. p. 185°) with a larger proportion of alcoholic ammonia, a second salt is obtained in crystals; this melts at 263—264°, and gives a pale-brown coloration with ferric chloride; on treatment with acids, the original salt is regenerated.

By the action of hydroxylamine in alkaline solution at ordinary temperatures on the compound $C_{12}H_{12}O_8$, a substance is obtained in colourless crystals; it is sparingly soluble in acids, readily dissolves in alkalis, and may be recrystallised from alcohol; it has the formula $C_{12}H_{10}O_8$, melts at 251—252°, and gives a deep-violet coloration with ferric chloride; the author regards it as a derivative of dihydroxyterephthalic acid, and points out that its formation affords an instance of hydroxylamine acting as an oxidising agent.

Experiments on the action of halogens and acids on the compound $C_{12}H_{12}O_8$ led to no definite result. The compound $C_{10}H_{10}O_7$, obtained from oxydehydracetic acid (see above), may also be prepared by cautiously heating the compound $C_{12}H_{12}O_8$ with hydrochloric acid; it is readily soluble in alcohol or chloroform, and is deposited in small, yellow, lustrous crystals which melt at 145° with decomposition, and sublime at lower temperatures; with ferric chloride, a dark-brown coloration is produced. On treatment with phenylhydrazine acetate, a complicated reaction occurs, and a substance is obtained crystallising in small, pale-yellow needles melting at 207—207·5°.

The third compound, $C_{10}H_8O_6$, is very sparingly soluble, and crystallises in groups of straw-coloured needles, which melt at 271° with decomposition; it may be prepared by the prolonged action of hydrochloric acid at 120° on the compound $C_{12}H_{12}O_8$. A deep-brown coloration is formed with ferric chloride.

The author discusses the constitution of dehydracetic acid and of oxydehydracetic acid; since the latter compound is a monocarboxylic acid and not an oxymethylacetopyronone, it follows that it contains a ring consisting of five atoms; the action of hydrochloric acid, above described, shows, however, that this ring cannot be a pentamethylene one; hence oxydehydracetic acid is either a ketofurfuran or a diketofurfuran derivative with one of the formulæ $\begin{matrix} O\text{---}CMe \\ | \\ CHAc\cdot CO \end{matrix}\!\!>\!C\cdot COOH$,

$$\begin{matrix} O\cdot C(CH_2Ac) \\ | \\ CH_2\text{---}CO \end{matrix}\!\!>\!C\cdot COOH, \text{ or } \begin{matrix} CH_2\text{---}O \\ | \\ CO\cdot CH_2 \end{matrix}\!\!>\!C{:}CAc\cdot COOH.$$

The work already accomplished does not enable the author to distinguish between these, but he is inclined to regard the first as the most probable. Assuming this to be correct, the compound $C_{12}H_{12}O_8$ (see above) is formed by the elimination of two acetyl groups from 2 mols. of the acid, and is, therefore, a *diacetodiketohexamethylenedicarboxylic acid*, $CO<\begin{matrix} CH(COOH)\cdot CHAc \\ CHAc\cdot CH(COOH) \end{matrix}>CO$; the second compound, $C_{10}H_{10}O_7$, formed from this by the elimination of an acetyl group, is *acetodiketohexamethylenedicarboxylic acid*,

$$CO<\begin{matrix}CH(COOH)—CH_2\\ CHAc\cdot CH(COOH)\end{matrix}>CO,$$

whilst the third, $C_{10}H_8O_6$, is probably a lactone,

$$O<\begin{matrix}CMe{:}C\cdot CO\cdot CH\cdot COOH\\ CO\cdot CH\cdot CO\cdot CH_2\end{matrix}.$$

J. B. T.

Dehydracetic Chloride. By F. Feist (*Ber.*, **25**, 335—339; compare preceding abstract).—Dehydracetic chloride, $C_8H_6O_2Cl_2$, does not react with potassium cyanide, mercuric cyanide, hydrogen cyanide, or phenyl cyanate. Similar negative results were also obtained by distillation of the chloride with zinc dust, by heating it with tin and hydrochloric acid, and by the action of alcoholic ammonia.

On treatment with alcoholic hydroxylamine at ordinary temperatures, reaction takes place accompanied by evolution of gas, and after removal of the alcohol and treatment of the residue with water, a compound is deposited in small, colourless, lustrous needles; this melts at 167° with decomposition, and is readily soluble in water, alcohol, and soda, but insoluble in carbon bisulphide. It reduces neutral silver solution on warming, and gives no coloration with ferric chloride; it probably has the formula $C_8H_{15}N_2ClO_6$, and appears to be a hydroxylamine salt of the compound immediately to be described.

On extracting with ether the aqueous filtrate from the preceding compound, two substances are obtained melting at 205° and 220° respectively. The former can also be prepared by heating the preceding compound at a temperature above its melting point, or by dissolving it in water, acidifying, and extracting the liquid with ether. The compound probably has the formula $C_8H_8NClO_3$; it is readily soluble in carbon bisulphide, does not reduce silver solution, and gives a dark, violet coloration with ferric chloride. The second compound (m. p. 220°) crystallises in lozenge-shaped plates, and yields no coloration with ferric chloride.

On reducing the first of the above compounds (m. p. 167°) with sodium amalgam, an acid is obtained in very small quantity, crystallising from alcohol in long needles which melt at 165°; it gives an olive-green coloration with ferric chloride, and contains nitrogen but no chlorine.

An amorphous compound of the formula $C_{16}H_{22}O_4$ is formed by the reduction of dehydracetic chloride with sodium amalgam; it decomposes at 202°, is insoluble in water or chloroform, dissolves readily in soda, and gives precipitates with several of the heavy metals.

The author concludes from these results that dehydracetic chloride is not a simple pyronone derivative. J. B. T.

Constitution of Dehydracetic Acid. By F. Feist (*Ber.*, **25**, 340—346; compare preceding abstracts).—The author criticises some recent papers of Collie on this subject (Trans., 1891, 172, 179, 607, 617); he considers that at present there is no proof of the formation of orcinol from dehydracetic acid. Since dehydracetic chloride is not

a simple derivative of dehydracetic acid, its formation does not show the presence of two hydroxyl groups in the latter compound; the balance of evidence points rather to the opposite conclusion, since dehydracetic acid behaves towards phosphoric acid as a monhydric alcohol.

When compounds containing the group $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO$ undergo condensation, it is usually the methylene rather than the methyl group which reacts; apart from this objection, Collie's explanation of the condensation of ethyl acetoacetate is inapplicable to ethyl benzoylacetate; the two reactions have, however, been shown to be strictly analogous. The recent synthesis of dehydracetic acid by Pechman (this vol., p. 296) from acetic anhydride and acetonedicarboxylic acid is then referred to, and is considered to be in itself sufficient proof of the formula $CO<\begin{matrix}CH:CMe\\CHAc{\cdot}CO\end{matrix}>O$.

The phosphate above mentioned has already been partially described; it crystallises in colourless, slender, lustrous needles, melts at 205° with decomposition, and is extremely stable towards hydrolysing agents. J. B. T.

Action of Phosphoric Chloride on Ethyl Oxalate. By A. Fauconnier (*Compt. rend.*, **114**, 122—123).—When a mixture of diethyl oxalate (1 mol.) and phosphoric chloride (2 mols.) is heated at 125° in a flask provided with a fractionating column, a violent reaction sets in, a large amount of ethyl chloride and a little hydrogen chloride being evolved; and when the temperature is raised to 150—155°, a mixture of ethyl chloride, phosphorus oxychloride, and oxalic chloride, $COCl{\cdot}COCl$, passes over, from which the last may be separated by fractionation. It is not practicable, however, to remove all the phosphorus oxychloride in this manner.

Impure *oxalic chloride*, as thus prepared, is a colourless, mobile liquid, which fumes strongly in the air, has a very irritating odour, recalling that of carbonyl chloride, and boils at about 70°. It is violently decomposed by water, with the formation of oxalic acid and hydrogen chloride, and by methyl alcohol, with the formation of dimethyl oxalate. Jn. W.

Dissociation in Dilute Solutions of Tartrates. By S. Sonnenthal (*Monatsh.*, **12**, 603—619).—With the object of ascertaining the influence of concentration on their rotatory power, the author has examined very dilute solutions of the normal and acid salts which tartaric acid forms with potassium, sodium, ammonium, and lithium. He finds that aqueous solutions of both normal and acid tartrates undergo a change of condition when a certain degree of dilution has been attained, and that this change occurs, in the case of solutions of the normal tartrates, when they contain between 0·4 and 0·3 per cent. of the salt, whilst in the case of solutions of the acid tartrates the change does not occur until between 0·3 and 0·2 per cent. of the salt is present. The commencement and the magnitude of this change depend on the nature of the salt-forming metal or radicle; the greater the atomic weight of the metal or the molecular weight of the radicle,

the greater the concentration at which the change begins, and the greater, also, the departure from the normal condition. The rapidity with which the change in condition occurs appears to depend entirely on the greater or less solubility of the salt in question.

The author regards the results he has obtained as evidence that the change in condition is due to dissociation, since relatively large quantities of water must be present in order to bring about the change, and further, because the greater the atomic weight of the metal, the sooner the change commences. G. T. M.

Cause of Acidity in Green Grapes. Tartromalic Acid. By C. Ordonneau (*Bull. Soc. Chim.* [3], **6**, 261—264). The author has isolated calcium tartromalate from green grape juice and from the wine resulting from grapes attacked by mildew. The salt separates, together with calcium tartrate, when the acid liquor is almost neutralised with lime, as asbestiform groups of needles, which are purified by successive recrystallisations. This double salt is a mixture of lævogyrate calcium tartrate and dextrogyrate calcium malate, and has the formula $CaC_4H_4O_6,CaC_4H_4O_5 + 6H_2O$; sulphuric acid converts it into calcium tartrate and calcium hydrogen malate. The author has prepared the double salt synthetically, by neutralising solutions of dextrogyrate hydrogen tartrate (1 mol.) and lævogyrate hydrogen malate (1 mol.) with an alkaline hydroxide, and subsequently precipitating with calcium acetate. Calcium tartromalate, on treatment with sulphuric acid, yields deliquescent crystals of tartromalic acid, and the author thinks this acid was mistaken by Erlenmeyer for glycollic acid and by Brunner for glyoxalic acid in their investigations on grape juice. Malic acid exists in some white wines to a greater amount than tartaric acid, the former disappearing as the grape ripens.

Calcium hydrogen malate, $Ca(C_4H_4O_5)_2 + 6H_2O$, dissolves in all proportions in boiling water; 100 grams water at 17° dissolve 1·25 grams; when heated at 100°, it melts in its water of crystallisation, and forms a gummy mass; when treated with boiling milk of lime, it is converted into calcium malate, and the author thinks that malic acid might be manufactured thus from grape juice and the lees of white wine by making use of this method. T. G. N.

β-Methylmalic Acid. By W. Wislicenus (*Ber.*, **25**, 196—203). —Just as inactive malic acid can be prepared by the reduction of ethyl oxalacetate (compare this vol., p. 147), β-methylmalic acid can be obtained by the reduction of ethyl methyloxalacetate. The acid obtained in this way is isomeric with the α-methylmalic acid or β-hydroxyglutaric acid prepared by Demarçay (*Compt. rend.*, **82**, 1337) from the cyanhydrin of ethyl acetoacetate.

β-Methylmalic acid, COOH·CHMe·CH(OH)·COOH (α-hydroxyglutaric acid), is prepared by gradually adding 3½ per cent. sodium amalgam (700—720 grams) to a mixture of ethyl methyloxalacetate (50 grams) and water (500 grams), with constant shaking, the solution being kept nearly neutral by frequently adding dilute sulphuric acid. When the whole of the amalgam has been decomposed, the neutralised solution is shaken with ether to extract ethyl β-methyl-

malate, and then evaporated to dryness; the residue contains sodium ethyl β-methylmalate and sodium β-methylmalate; the former can be extracted with boiling alcohol, from which it is deposited on cooling in colourless needles, and the β-methylmalic acid can then be isolated by means of its lead salt, after first precipitating the sulphuric acid present with barium hydroxide.

β-Methylmalic acid, prepared from its lead salt, is a thick, colourless syrup, miscible with water and alcohol, and readily soluble in ether. The *lead* salt, $C_5H_6O_5Pb + H_2O$, is sparingly soluble in hot water, from which it separates almost completely, on cooling, as a colourless, amorphous powder; it loses the whole of its water at 110°. The *silver* salt, $C_5H_6O_5Ag_2$, is a colourless, amorphous compound, very sparingly soluble in hot, and insoluble in cold water; it is moderately stable in the light, but is decomposed on prolonged boiling with water. The *calcium* salt, $C_5H_6O_5Ca + 3H_2O$, is amorphous, and moderately easily soluble in hot water; it does not become completely anhydrous at 140°. The *dihydrazide*, $C_{17}H_{20}N_4O_3$, is crystalline, melts at 231—232°, and is moderately easily soluble in hot alcohol and glacial acetic acid, but only very sparingly in cold water, alcohol, and ether; its solution in concentrated sulphuric acid gives a red coloration on the addition of ferric chloride. The *ethyl* salt, $C_9H_{16}O_5$, is a thick, colourless oil, boiling at 250° under a pressure of 745 mm. (at 175°, 78 mm.; 143°, 21 mm.; 138°, 17 mm.). The *sodium ethyl salt*, $C_7H_{11}O_5Na$ (see above) sinters together at 161°, melts at 166—167°, and is very readily soluble in water; its aqueous solution gives, with silver, cadmium, and mercurous salts, colourless precipitates, which crystallise from hot water in needles, and, with lead acetate, a colourless, amorphous precipitate. F. S. K.

Additive Products of Ethyl Sodacetoacetate and Sodiomalonate with Ethereal Salts of Unsaturated Acids. By A. Michael and O. Schulthess (*J. pr. Chem.* [2], **45**, 55—63; compare Abstr., 1891, 914).—The ethyl salts, $C_3H_4(COOEt)_4$, obtained by the action of ethyl sodiomalonate on ethyl fumarate and ethyl maleate, respectively, are apparently identical; they boil at 202—203° at 16—17 mm. When heated with potassium hydroxide solution, they yield potassium tricarballylate and potassium carbonate; with barium hydroxide solution, the barium salt of the corresponding tetracarboxylic acid is obtained without the elimination of carbonic anhydride, and from this salt the acid may be obtained as a colourless syrup, which evolves carbonic anhydride and yields tricarballylic acid (m. p. 155—156°) when heated at 120—130°.

The reaction between ethyl citraconate and ethyl sodiomalonate yields a colourless oil, $C_4H_6(COOEt)_4$, which distils at 204—205° at 20 mm. Another sample distilled at 201° at 17 mm. It distils at 300° at the ordinary pressure with partial decomposition. The barium salt (with 2 mols. H_2O) of the corresponding acid was prepared by hydrolysis with barium hydroxide, and from this the acid itself was obtained. The acid forms slightly coloured crystals, which decompose at 120—130° with loss of carbonic anhydride; the change has not been further investigated.

The additive product obtained from ethyl mesaconate and ethyl sodiomalonate boils at 204—206° at 20 mm., and is apparently identical with that obtained from ethyl citraconate.

The ethereal salt, $C_{16}H_{26}O_8$, from ethyl itaconate and ethyl sodiomalonate, boils at 211·5—212·5° at 17 mm., and the same product is obtained from ethyl itachloropyrotartrate (b. p. 139° at 17—18 mm.) and ethyl sodiomalonate. The treatment of these two ethyl tetracarboxylates with ammonia produces a crystalline amide, which melts with decomposition at 250°. The ethyl tetracarboxylate obtained from ethyl mesaconate gave no amide, whilst that from ethyl citraconate gave very little, which was traced to the presence of itaconic anhydride in the citraconic anhydride used in the preparation of the ethyl salt.

The action of ethyl allylmalonate on ethyl sodiomalonate gave no additive product. A. G. B.

Trimethylenetrisulphone. By R. Camps (*Ber.*, **25**, 233—247). —The *sodium* derivative of trimethylenetrisulphone (compare Baumann and Camps, Abstr., 1890, 478) is deposited in transparent, rhombic plates, when the trisulphone is dissolved in warm 10 per cent. soda, and the solution then allowed to cool; it has the composition $C_3H_5NaS_3O_6 + H_2O$, and decomposes on exposure to the air. The *potassium* derivative, $C_3H_5KS_3O_6$, crystallises in small, compact prisms, and is only sparingly soluble in cold water. The *lithium* derivative, $C_3H_5LiS_3O_6 + 4H_2O$, and the *barium* derivative,

$$(C_3H_5S_3O_6)_2Ba + 4H_2O,$$

crystallise in slender needles. The *silver* derivative, $C_3H_5AgS_3O_6$, crystallises from hot water in slender needles, and is moderately stable in the light.

When the sodium derivative of trimethylenetrisulphone (1 mol.) is treated with methyl iodide (1 mol.) in dilute alcoholic solution, a mixture of the *di-* and *tri-methyl*-derivatives is obtained, a considerable quantity of the trisulphone remaining unchanged; the two methyl derivatives cannot be easily isolated in a pure condition, owing to the similarity of their behaviour towards solvents, but they can be partially separated by fractional crystallisation of their potassium derivatives; both compounds are soluble in hot water, alcohol, and glacial acetic acid, and sublime without melting.

When molecular proportions of ethyl iodide and the sodium derivative of trimethylenetrisulphone react in dilute alcoholic solution, a mixture of the *mono-* and *di-ethyl* derivatives is obtained, but the two compounds could not be separated.

Hexethyltrimethylenetrisulphone, $C_3Et_6S_3O_6$, is obtained, together with the tetrethyl derivative, when an alcoholic soda solution of the trisulphone is heated with excess of ethyl iodide at 100°; the two compounds are separated by treatment with soda, in which the hexethyl derivative is insoluble. It crystallises from alcoholic benzene in long needles, melts at 208°, and is almost insoluble in water, and only sparingly soluble in hot alcohol, chloroform, ethyl acetate and acetone, but more readily in benzene; it crystallises unchanged from hot, concentrated sulphuric acid, and is not decomposed by boiling alkalis. The

tetrethyl derivative, $C_3H_2Et_4S_3O_6$, crystallises from hot alcoholic benzene in lustrous prisms melting at 175°.

Dipropyltrimethylenetrisulphone, $C_3H_4Pr_2S_3O_6$, is formed when a dilute alcoholic solution of molecular proportions of propyl iodide and the sodium derivative of the trisulphone is heated for 24 hours; it crystallises from alcohol in slender needles, melts at 297°, sublimes above 300° with partial decomposition, and is only sparingly soluble in ether, benzene, and chloroform, but rather more readily in boiling alcohol and hot glacial acetic acid. The *hexapropyl* derivative, $C_3Pr_6S_3O_6$, crystallises from alcohol in compact prisms, melts at 133°, and is moderately easily soluble in alcohol, benzene, and hot glacial acetic acid, but insoluble in boiling soda.

Tetrabenzyltrimethylenetrisulphone, $C_3H_2S_3O_6(CH_2Ph)_4$, is obtained when the trisulphone is heated with excess of benzyl chloride and alcoholic soda for half an hour at 100°; it crystallises from glacial acetic acid in slender, colourless needles, melts at 171—172°, and is insoluble in soda.

Hexabromotrimethylenetrisulphone, $C_3Br_6S_3O_6$, is produced when the trisulphone is rubbed to a paste with water, and bromine-water added until a permanent coloration is produced; it crystallises from dilute acetic acid in compact prisms, melts at 146°, and decomposes at a higher temperature. It dissolves freely in benzene, ether, chloroform, and acetone, but is almost insoluble in water; it is slowly decomposed by hot alcohol, more quickly by warm ammonia, alkalis, and alkali carbonates, with formation of sulphuric acid and hydrobromic acid.

The *hexachloro*-derivative, $C_3Cl_6S_3O_6$, prepared by passing chlorine-water into water containing the trisulphone in suspension, in presence of direct sunlight, crystallises from glacial acetic acid in lustrous prisms, melts at 252° with decomposition, and is soluble in benzene, ether, and chloroform, but insoluble in water; it resembles the hexabromo-derivative in its behaviour with alcohol and alkalis.

F. S. K.

Trimethylenedisulphonesulphide. By R. Camps (*Ber.*, **25**, 248—257).—*Trimethylenedisulphonesulphide*, $SO_2<\begin{matrix}CH_2—S\\CH_2\cdot SO_2\end{matrix}>CH_2$, is obtained, together with trimethylenetrisulphone, in the oxidation of trithioformaldehyde with potassium permanganate in presence of dilute sulphuric acid (compare preceding abstract, also Abstr., 1890, 478); the mixture of the two compounds is dissolved in excess of hot potash, the crystalline potassium derivative of the trisulphone separated, the mother liquor acidified with hydrochloric acid, and the precipitated trimethylenedisulphonesulphide separated from small quantities of the trisulphone by recrystallisation from boiling water. It forms slender needles, is only sparingly soluble in hot glacial acetic acid, alcohol, and benzene, and does not melt at 340°; on oxidation with potassium permanganate in dilute sulphuric acid solution at the ordinary temperature, it is slowly converted into the trisulphone. It is slowly decomposed by hot concentrated nitric acid with formation of sulphurous acid and sulphuric acid, and when

heated with concentrated sulphuric acid it undergoes complete decomposition with separation of sulphur and evolution of sulphurous anhydride; it dissolves freely in ammonia, alkalis, and alkali carbonates, but separates from the concentrated solutions unchanged, and, on prolonged heating with alkalis, it undergoes decomposition. The *dimethyl* derivative, $C_3H_4Me_2S_3O_4$, is formed when the disulphonesulphide is warmed with alkali and excess of methyl iodide in dilute alcoholic solution; it crystallises from glacial acetic acid in lustrous, slender needles, melts at 319°, and is readily soluble in hot alcohol and benzene, but only sparingly in hot water, and insoluble in alkalis; it is not acted on by bromine in hot acetic acid solution.

Dimethyltrimethylenetrisulphone, $C_3H_4Me_2S_3O_6$, is formed when dimethyltrimethylenedisulphonesulphide is oxidised with potassium permanganate; it crystallises from acetic acid in compact needles, does not melt at 340°, and is only very sparingly soluble in hot water, ether, benzene, and chloroform, but rather more readily in boiling alcohol and glacial acetic acid; when treated with methyl iodide in alkaline alcoholic solution, it is converted into hexamethyltrimethylenetrisulphone. The *tetrabromo*-derivative, $C_3Br_4Me_2S_3O_6$, crystallises from glacial acetic acid in slender needles, melts at 231° with decomposition, and is sparingly soluble in most ordinary solvents; it is decomposed by ammonia and alkalis with formation of sulphuric and hydrobromic acids.

Ethyltrimethylenedisulphonesulphide, $C_3H_5EtS_3O_4$, crystallises from glacial acetic acid in lustrous needles, melts at 280°, and is only sparingly soluble in hot water, but more readily in boiling benzene, ether, alcohol, and glacial acetic acid; it is decomposed by boiling nitric acid and by concentrated sulphuric acid, but it crystallises unchanged from boiling soda. The *bromo*-derivative, $C_3H_4BrEtS_3O_4$, crystallises from glacial acetic acid in needles, melting at 204° with decomposition.

Ethyltrimethylenetrisulphone, $C_3H_5EtS_3O_6$, prepared by oxidising the preceding compound with 5 per cent. potassium permanganate in dilute sulphuric acid solution, crystallises from glacial acetic acid in slender, lustrous needles, does not melt at 340°, and is only sparingly soluble in boiling alcohol and hot water. The *pentabromo*-derivative, $C_3Br_5EtS_3O_6$, crystallises from glacial acetic acid in slender needles, melts at 221° with decomposition, and is only very sparingly soluble in most ordinary solvents; it is readily decomposed by warm ammonia and warm alkalis. The *pentamethyl* derivative, $C_3Me_5EtS_3O_3$, separates from alcoholic benzene in compact needles, melts at 241°, and is soluble in glacial acetic acid, ether, and chloroform, but insoluble in water; it is very stable towards boiling alkalis, and crystallises unchanged from hot concentrated sulphuric acid.

Dibromotrimethylenedisulphonesulphide, $C_3H_4Br_2S_3O_4$, is formed when excess of bromine is added to a hot saturated solution of the disulphonesulphide in 90 per cent. acetic acid, from which it crystallises after some time in short, compact, lustrous prisms; it does not melt at 330°, and is almost insoluble in water, and is only sparingly soluble in benzene and ether. The *hexabromo*-derivative, $C_3Br_6S_3O_4$, prepared by adding excess of bromine to an aqueous solution of the disulphone-

sulphide, saturated at 30—40°, crystallises from glacial acetic acid in nacreous, yellow plates, melts at 132°, and decomposes at a higher temperature; it is readily soluble in hot glacial acetic acid and benzene, and, like the dibromo-derivative, is decomposed by warm alcohol and by alkalis; on prolonged boiling with glacial acetic acid, it is converted into the dibromo-derivative. F. S. K.

Reduction of Benzene Hexachloride. By J. Meunier (*Compt. rend.*, **114**, 75—76).—Benzene hexachloride, when reduced with glacial acetic acid and zinc, yields benzene perfectly free from thiophen, but benzene hexahydride is not formed. C. H. B.

Friedel-Crafts Synthesis. By M. Schöpff (*Ber.*, **24**, 4252).—The author was unaware when he published his paper (this vol., p. 337) that a similar conclusion had been arrived at by Claus (Abstr., 1891, 911), namely, that by treating certain halogen derivatives of benzene with acid chlorides in the presence of aluminium chloride, the acidyl group takes the para-position relatively to the halogen; the author found, however, that when this position is already substituted, no reaction occurs, whereas Claus stated that in this case the acidyl group takes the ortho-position relatively to the halogen, although he had not isolated the ketone in the pure state. The author is willing to discontinue the further study of this subject, as also that of parabromometatoluic acid and parabromisophthalic acid; he has, however, been engaged for a considerable time in investigating the amido- and anilido-derivatives of the latter compound. A. R. L.

First Reduction Products of the Nitro-group. By C. Willgerodt (*J. pr. Chem.* [2], **45**, 145—153).—A further examination of the reduction product obtained by the action of potassium iodide on picryl chloride in alcoholic solution, which the author has described as dinitrosonitrophenol (Abstr., 1891, 688), shows that it is not a dinitrosophenol, but the isomeric hydroxylamine compound *dinitrophenylenehydroxylamine*, $C_6H_2(NO_2)_2{:}NOH$. It is extremely stable towards acids and acid chlorides, and can be boiled with phosphoric chloride, acetic chloride, and hydrochloric acid without decomposing. If heated to boiling with sulphuric acid, it is precipitated unchanged on the addition of water in beautiful white crystals. When heated with alcoholic potash, it is decomposed with formation of an ethylamine, and with aqueous potash it yields ammonia. It quickly reduces Fehling's solution on heating. The *ammonium* salt is obtained by leading ammonia into an ethereal solution of the compound, and has a beautiful green lustre like magenta crystals. The *silver* and *lead* salts are obtained as orange-red precipitates on adding silver or lead nitrate to a solution of the ammonium salt, and when dry are stable in light and air. The silver salt explodes violently when treated with fuming nitric acid. The lead salt also explodes when heated with sulphuric acid. With aniline, dinitrophenylenehydroxylamine yields an additive compound of the formula $C_6H_3N_3O_5,NH_2Ph$,

which crystallises in beautiful red prisms or needles, melts at 125—126°, and slowly loses aniline when exposed to the air, more quickly on heating. The paratoluidine compound has the formula $(C_6H_3N_3O_5)_3,(C_6H_4Me{\cdot}NH_2)_2$, crystallises in dark bluish-brown needles, and melts at 101—102°.

α-Nitronaphthalene, when reduced with potassium iodide and formic acid in a sealed tube at 230—270°, yields a white compound which melts at about 130°, and does not reduce Fehling's solution.

Metadinitrobenzene, when heated with potassium iodide and acetic acid in a sealed tube at 200°, yields paranitraniline. If, however, it is reduced in alcoholic solution with stannous chloride without the addition of hydrochloric acid, it yields dinitrosoazobenzene.

The author is engaged in examining the action of alcoholic stannous chloride without the addition of acid on a series of aromatic nitro-derivatives. E. C. R.

Propoxy-derivatives of Cumonitrile. By M. Fileti and V. Abbona (*Gazzetta*, **21**, ii, 399—402).— The authors had previously failed to obtain a propoxy-derivative of cumonitrile by treating a strongly alkaline solution with potassium permanganate, the cyanogen radicle being attacked under these conditions.

Propoxybenzonitrile, $OPr{\cdot}C_6H_4{\cdot}CN$, has now been isolated by leaving a mixture of water (200 c.c.), potassium permanganate (6·4 grams), and cumonitrile (4 grams) for 18 to 20 days at the ordinary temperature, with occasional agitation, decolorising the product with alcohol, distilling off the unaltered cumonitrile, and concentrating. The propoxy-compound separates as an oily liquid which, after crystallisation from light petroleum, forms lustrous, flattened needles, melts at 51—52°, and dissolves readily in alcohol, ether, and water. On boiling with potash (50 per cent.), it is hydrolysed, propoxybenzoic acid (m. p. 155—156°) being formed.

Propoxybenzamide, $OPr{\cdot}C_6H_4{\cdot}CONH_2$, is obtained by leaving a mixture of cumonitrile and potassium permanganate in the proportions given before, with water (800 c.c.) and potash (2·4 grams) for 10 to 12 days, decolorising with alcohol, and concentrating. The amide crystallises out in long needles, melts when pure at 144—145°, dissolves readily in alcohol and sparingly in benzene and ether, but is insoluble in light petroleum. On boiling with 50 per cent. solution of potash, it is converted into propoxybenzoic acid. A mercury derivative, $(C_{10}H_{12}O_2N)_2Hg$, forms minute crystals melting at about 240°. S. B. A. A.

Bromamidocarvacrol. By G. Mazzara (*Gazzetta*, **21**, ii, 378—380).—The author previously found (Abstr., 1890, 884), that, on reducing bromonitrosocarvacrol, amidobromocarvacrol hydrochloride was formed, and from this the base was prepared as a red liquid, setting in a few days to an amorphous mass which melted at 60°. The melting point of the compound, which is lower than that of the corresponding thymol derivative, and its amorphous character led the author to suspect its purity. On preparing it by the action of fuming

hydrobromic acid on nitrosocarvacrol, it crystallises from light petroleum in yellow needles with a violet tinge, and melts at 136—137°. An unsuccessful attempt was made to oxidise the base with ferric chloride, and convert it into the bromothymoquinone melting at 54°, the product resisting purification, and melting at a low temperature.

S. B. A. A.

Penta-derivatives of Benzene. By R. Nietzki and L. Kurtenacker (*Ber.*, **25**, 282—285).—When Habermann's trinitrodimethylquinol is heated for some hours in a sealed tube at 110—120° with alcoholic ammonia, it decomposes in a manner analogous to the diethyl derivative (Abstr., 1883, 466), and yields *dinitrodiamidoanisoïl*, $C_6H(NO_2)_2(NH_2)_2{\cdot}OMe$, which crystallises from glacial acetic acid in red leaflets having a blue shimmer, and melts at 250°. It dissolves in boiling aqueous alkalis with evolution of ammonia, and on adding acid to the solution, a compound is precipitated which crystallises from dilute alcohol in golden-yellow leaflets, melts at 130°, and is a *dinitrodihydroxyanisoïl*, $C_6H(NO_2)_2(OH)_2{\cdot}OMe$; the *barium* salt crystallises in reddish-yellow leaflets. When the dihydroxy-derivative is reduced with tin and hydrochloric acid, a product is obtained which does not react with orthodiketones. When the above-described dinitrodiamidoanisoïl is reduced with tin and hydrochloric acid, and sulphuric acid and alcohol are added to the resulting solution, a sparingly soluble sulphate, $2OMe{\cdot}C_6H(NH_2)_4{,}3H_2SO_4$, is precipitated in colourless leaflets. The tetramido-derivative reacts with orthodiketones, forming diquinoxalines thus:—it forms a compound, $OMe{\cdot}C_6H(N_2C_{14}H_{10})_2$, with benzile which crystallises in orange-yellow needles, is sparingly soluble in glacial agetic acid, and melts at 242°; and a compound, $OMe{\cdot}C_6H(N_2C_3H_4O)_2$, with pyruvic acid, which dissolves in alkalis, and is reprecipitated in orange-yellow flocks on the addition of an acid, but is practically insoluble in indifferent solvents. The formation of diquinoxalines indicates that in the tetramido-derivative, the four NH_2 groups are in consecutive positions. A symmetrical constitution is indeed excluded by that of the trinitrodimethylquinol $[OMe)_2 : (NO_2)_3 = 1 : 4 : 2 : 3 : 5]$; it follows therefore that the methoxyl group in position 4 in the latter is the one displaced by NH_2, and since the compound formed by reducing dinitrodihydroxyanisoïl does not yield an azine, it is probably the NO_2 group in position 2 which is simultaneously displaced by NH_2; the constitution of the diamidodinitroanisoïl would then be

$$[OMe : (NH_2)_2 : (NO_2)_2 = 1 : 2 : 4 : 3 : 5].$$

A. R. L.

Condensation Products of Dicyanophenylhydrazine with Aliphatic Aldehydes. By J. A. Bladin (*Ber.*, **25**, 183—188).—Aliphatic aldehydes react with dicyanophenylhydrazine in exactly the same manner as the aromatic aldehydes (Abstr., 1889, 702), yielding condensation products which are readily converted by oxidising agents into triazole derivatives.

Acetaldehyde and dicyanophenylhydrazine readily react in alcoholic solution, forming *ethylidenedicyanophenylhydrazine*,

$$NC\cdot C(NH)\cdot NPh\cdot N{:}CHMe,$$

which crystallises from light petroleum in pale-yellow plates, and melts at 95·5—96·5°. By the action of oxidising agents, such as silver nitrate and ferric chloride, it is quickly converted into phenylmethylcyanotriazole.

Œnanthaldehyde unites with dicyanophenylhydrazine, forming the condensation product $NC\cdot C(NH)\cdot NPh\cdot N{:}CH\cdot[CH_2]_4\cdot CH_2Me$; this was oxidised with ferric chloride to phenylhexylcyanotriazole, and the latter at once converted into *phenylhexyltriazolecarboxylic acid*, $C_6H_{13}\cdot C_2N_3Ph\cdot COOH$, which crystallises from water in silvery plates, and melts at 126° with slight evolution of gas. Its *methyl* and *ethyl* salts are colourless oils; the alkali salts are readily soluble in water; the *silver* salt is an almost insoluble precipitate, and the *copper* salt, with 1 mol. H_2O, a pale-blue, microcrystalline precipitate. The *hydrochloride* crystallises in colourless, matted needles which are decomposed by water; the *amide*, $C_6H_{13}\cdot C_2N_3Ph\cdot CONH_2$, obtained by the action of ammonia on the ethyl salt, crystallises from benzene in lustrous plates containing benzene of crystallisation, which is evolved when the crystals are melted, the substance, after solidification, remelting at 82—82·5°. The *thiamide*, $C_6H_{13}\cdot C_2N_3Ph\cdot CSNH_2$, forms sulphur-yellow plates, and melts at 76—77°. H. G. C.

Action of Ethyl Acetoacetate on Dicyanophenylhydrazine. By J. A. Bladin (*Ber.*, 25, 189—196).—When dicyanophenylhydrazine is warmed with twice its weight of ethyl acetoacetate, alcohol is evolved; the product, after distilling off the excess of ethyl acetoacetate, consists of a crystalline mass saturated with an oily substance. On treatment with alcohol, the oily portion and some of the crystals dissolve, leaving a residue which is almost insoluble in cold alcohol, but crystallises from the hot liquid in small, lustrous plates. It has the composition $C_{12}H_{12}N_4O_2$, melts at 208—209°, and has the properties of an acid.

The portion of the original product soluble in alcohol consists of phenylmethylcyanotriazole, and an oil which was not obtained pure, but which, on treatment with alkalis, yields the acid $C_{12}H_{12}N_4O_2$, described above, and is therefore probably its ethyl salt. The formation of this ethyl salt and of the acid is readily understood, the ordinary hydrazone condensation taking place between ethyl acetoacetate and dicyanophenylhydrazine, the ethyl salt being partially hydrolysed at the temperature employed. The formation of phenylmethylcyanotriazole, which is always obtained in smaller quantity, probably takes place as follows: the ethyl acetoacetate decomposes to some extent on boiling, and the acetic acid set free converts the dicyanophenylhydrazine into the acetyl derivative

$$NC\cdot C(NH)\cdot NPh\cdot NH\cdot COMe,$$

which then loses water, forming phenylmethylcyanotriazole; this would be exactly analogous to the reaction between dicyanophenyl-

hydrazine and pyruvic acid (Abstr., 1887, 138). A further possibility is that it is formed from the acid $C_{12}H_{12}N_4O_2$ by elimination of acetic acid, but this compound is very stable, and, although decomposed by boiling acids and alkalis, does not yield phenylmethylcyanotriazole among the products of decomposition.

A number of derivatives of the acid $C_{12}H_{12}N_4O_2$ have been prepared; the *ammonium* salt, $C_{12}H_{11}N_4O_2{\cdot}NH_4$, forms spherical groups of crystals, and the *potassium* salt, $C_{12}H_{11}N_4O_2K$, a matted mass of slender, colourless needles, both salts being very unstable. The acid is converted by nitrous acid into an *isonitroso*-compound,

$$NC{\cdot}C(NH){\cdot}NPh{\cdot}N{:}CMe{\cdot}C(NOH){\cdot}COOH,$$

which, after recrystallisation from alcohol, melts at 217—218°, forming a brown oil; it dissolves very sparingly in water, but readily in aqueous alkalis.

When the acid is boiled with dilute hydrochloric acid or potash, the imido-group is replaced by oxygen, with formation of the compound $NC{\cdot}CO{\cdot}NPh{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOH$, which crystallises from alcohol in flat, colourless needles, melts at 187—188° with evolution of gas, and is sparingly soluble in water. With nitrous acid, it yields the *isonitroso*-derivative $NC{\cdot}CO{\cdot}NPh{\cdot}N{:}CMe{\cdot}C(NOH){\cdot}COOH$, which forms small, colourless prisms, readily soluble in alcohol, but sparingly in water, and melts at 209° with decomposition.

H. G. C.

Stereoisomeric Nitrogen Compounds other than Oximes. By K. Auwers and V. Meyer (*Ber.*, **24**, 4225—4230).—Hantzsch and Kraft (this vol., p. 338) describe two isomeric hydrazones of anisyl phenyl ketone, which they regard as stereochemical isomerides, and represent by formulæ similar to those ascribed to the isomeric oximes of benzile by Hantzsch and Werner. The authors point out that Hantzsch and Kraft state in support of the structural identity of the two hydrazones, that they exhibit the same reactions, without, however, giving any details as to these reactions, and that they are similar in physical properties, an observation which has no significance when it is considered that the isomeric benziloximes are compounds differing widely in physical properties. The authors further contend that stereoisomeric hydrazones can be represented by formulæ similar to those assigned by them to derivatives of hydroxylamine (Abstr., 1890, 1263), thus:— $X{\cdot}C{\cdot}Y$ (=) N (–) $H{\cdot}N{\cdot}Ph$ and $X{\cdot}C{\cdot}Y$ (=) N (–) $N{<}{H \atop Ph}$ (compare Abstr., 1890, 1117; 1891, 302).

A. R. L.

Oximes and so-called Stereochemistry. By A. Claus (*J. pr. Chem.* [2], **45**, 1—20).—The author replies to Auwers and Meyer (this vol., p. 186), who have criticised his previous paper on the subject (this vol., p. 50), and maintains his former position. The paper contains no new facts.

A. G. B.

Amidotolyloxamic and Urethanotolyloxamic Acids. By U. Schiff and A. Vanni (*Gazzetta*, **21**, ii, 409—451). Amidotolyloxamethane was prepared by Tiemann (*Ber.*, 1870, 222) by boiling a solution of tolylenediamine and ethyl oxalate in absolute alcohol. The action proceeds much more rapidly if aqueous alcohol is employed. Tolylenediamine (40 parts) and ethyl oxalate (50 parts) are dissolved in 93—95 per cent. alcohol (170—200 parts), and boiled in a reflux apparatus for several days. From time to time the liquid is cooled, the crude amidotolyloxamethane (44 parts) which separates is filtered off, and the filtrate again heated, after adding a little ethyl oxalate and alcohol. The alcohol and ethyl oxalate are finally distilled off, leaving a syrupy residue, which partially solidifies after a time. On extracting this with dilute hydrochloric acid, amidotolyloxamethane dissolves, and may be precipitated by sodium carbonate solution; the residue, insoluble in acid, consists of tolylenedioxamethane and amidotolyloxamic acid. Amidotolyloxamethane is also formed on boiling a concentrated solution of tolylenediamine and oxamethane in molecular proportion in absolute alcohol.

Acetamidotolyloxamethane, $NHAc{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OEt$, is prepared by dissolving amidotolyloxamethane in boiling acetic anhydride. It crystallises from boiling alcohol in colourless scales, and melts at 192°.

Thiocarbaniltolyloxamethane, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OEt$, is formed when a solution in absolute alcohol of amidotolyloxamethane and phenylthiocarbamide in molecular proportion is heated for a short time. On cooling, it separates in colourless prisms which, after crystallisation from alcohol, melt at 154—155°. The alcoholic mother liquors yield a small quantity of a yellow powder, which melts at 138°, and on fusion with caustic potash gives aniline and potassium oxalate. This is probably formed from the preceding compound by elimination of alcohol, and may be represented as $C_7H_6{<}^{NH{\cdot}C_2O_2}_{NH-CS}{>}NPh$. When the thiocarbaniltolyloxamethane is crystallised from alcohol, the mother liquor yields two crystalline compounds, one of which is in the form of bright scales containing sulphur and melting at 136—138°. The small quantities of these substances obtained precluded further examination.

An alcoholic solution of amidotolyloxamethane and carbon bisulphide, when heated in a closed tube at 100° for two days, yields much hydrogen sulphide. A crystalline substance containing sulphur is also obtained, but was not further studied owing to the difficulty of purifying it.

When amidotolyloxamethane is heated at 180° for a day, alcohol is eliminated, and the dark brown residue is found to be partially soluble in boiling alcohol, leaving a yellow powder probably consisting of *tolyleneoxamide*,

$$C_7H_6{<}^{NH}_{NH}{>}C_2O_2 \text{ or } C_7H_6{<}^{NH{\cdot}C_2O_2{\cdot}NH}_{NH{\cdot}C_2O_2{\cdot}NH}{>}C_7H_6.$$

It is insoluble in the ordinary solvents, but dissolves in concentrated sulphuric acid; on adding nitric acid to this solution, it turns blood-

red, and yields a nitro-derivative which crystallises from boiling alcohol in yellow needles. Tolyleneoxamide carbonises and evolves gas at about 266°. It dissolves slowly in boiling aqueous potash, without evolution of ammonia. It is also formed on boiling amidotolyloxamethane with water for eight hours, and, together with a little amidotolyloxamic acid, on heating tolylenediamine oxalate at 160°.

An alcoholic solution of tolylenediamine and ethyl malonate, heated in a closed tube at 120°, yields a small quantity of a substance which separates from boiling acetic acid in minute, colourless needles, and is sparingly soluble in boiling alcohol. It is probably *tolylenemalonamide*, $C_7H_6<^{NH\cdot CO}_{NH\cdot CO}>CH_2$. When its solution in concentrated sulphuric acid is treated with nitric acid, a nitro-derivative crystallising in yellow needles is obtained.

Lussy (this Journal, 1875, 254) prepared tolylenediurethane by dropping ethyl chlorocarbonate into a cooled alcoholic solution of tolylenediamine. The authors find that the mother liquor on concentration deposits first tolylyenediamine hydrochloride and then *amidotolylurethane hydrochloride*. The mother liquor, after further concentration, is dissolved in water and potash added, when a mixture of tolylenediamine and *amidotolylurethane*, $NH_2\cdot C_6H_3Me\cdot NH\cdot COOEt$, is precipitated; this crystallises from alcohol in long, flat needles of pearly lustre. It melts at 91°, and is very soluble in hot alcohol, less so in ether and hot water. Its hydrochloride is very soluble in water and crystallises badly. The *platinochloride* forms straw-coloured crystals. Amidotolylurethane is not altered by heating with alcoholic ammonia in a closed tube at 120°; when heated for several hours with aniline, it yields diphenylcarbamide and tolylenediamine. Attempts to prepare it from tolylenediurethane by heating with alcoholic ammonia in a sealed tube at 140° or by boiling with aniline failed.

Thiocarbaniltolylurethane, $NHPh\cdot CS\cdot NH\cdot C_6H_3Me\cdot NH\cdot COOEt$

$$[Me : NH\cdot CS : NH\cdot CO = 1:2:4],$$

is prepared by boiling for a short time an alcoholic solution of amidotolylurethane and phenylthiocarbamide in molecular proportion. It separates from alcohol in colourless prisms melting at 154—155°. If excess of phenylthiocarbamide is used and the boiling prolonged, *diphenylthiocarbamide*, $CS(NHPh)_2$, is obtained, together with other compounds containing sulphur which could not be separated. The former crystallises from alcohol in lustrous scales, melts at 148—150°, and yields aniline when fused with potash.

An alcoholic solution of tolylenediurethane and phenylthiocarbamide when heated gives a mixed product, one of the constituents of which is *phenylthiourethane*, $OEt\cdot CS\cdot NHPh$, a well-crystallised substance melting at 64—65°. A little diphenylthiocarbamide and an oil, which is probably ethyl carbonate, together with other compounds containing sulphur, are also present. The reaction is represented by the equation $C_7H_6(NH\cdot COOEt)_2 + 4CSNPh + 4EtOH = 2CO(OEt)_2 + 2EtO\cdot CS\cdot NHPh + C_7H_6(NH\cdot CS\cdot NHPh)_2$. The latter substance, tolylenedithiophenylcarbamide, decomposes at once into tolylenethiocarbamide and diphenylthiocarbamide.

Oxamethanotolylurethane, $OEt{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}COOEt$

$[Me : NH{\cdot}C_2O_2 : NH{\cdot}CO = 1 : 2 : 4]$,

is prepared by boiling a concentrated alcoholic solution of amidotolylurethane with a little more than the equivalent proportion of ethyl oxalate. It is deposited on concentrating the solution, and when recrystallised from alcohol is obtained in long, colourless prisms which melt at 128°. Its alcoholic solution, on treatment with alcoholic ammonia, deposits small, colourless prisms of *oxamidotolylurethane*, $NH{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}COOEt$, which melts at 223°, and gives off ammonia when heated with dilute caustic potash.

Urethanotolyloxamethane, $COOEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OEt$

$[Me : NH{\cdot}CO : NH{\cdot}C_2O_2 = 1 : 2 : 4]$,

is prepared by slowly dropping ethyl chlorocarbonate (2·5 c.c.) into an ice-cold solution of amidotolyloxamethane (5 grams) in absolute alcohol. The green, fluorescent liquid is evaporated to dryness, and the unaltered amidotolyloxamethane hydrochloride extracted by boiling with very dilute hydrochloric acid. The urethanotolyloxamethane remains undissolved, and crystallises from dilute alcohol in colourless, spherical aggregates melting at 131°. It is very soluble in alcohol, sparingly so in water. On treatment with cold alcoholic ammonia, it yields colourless crystals of *urethanotolyloxamide*, $COOEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}NH_2$, which melts at 209°.

Paranitrotolylurethane, $COOEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}NO_2$ $[CH_3 : NH : NO_2 = 1 : 2 : 4]$, is prepared by the action of ethyl chlorocarbonate on nitrotoluidine. It crystallises in colourless needles, melts at 137°, and is very soluble in alcohol and ether, less so in boiling water. Its alcoholic solution, when boiled with ethyl oxalate, yields *nitrotolyloxamethane;* this can be converted into *nitrotolyloxamide* by treatment with cold alcoholic ammonia.

Paramidotolylurethane, $COOEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH_2$, is formed on reducing paranitrotolylurethane (1 mol.) in boiling hydrochloric acid solution by means of stannous chloride (3 mols.). After the addition of much water, the tin is removed by hydrogen sulphide, the filtered solution concentrated, excess of sodium carbonate solution added, and the liquid extracted with ether. The residue left on evaporating the ethereal solution, is purified by conversion into the hydrochloride, treatment with sodium carbonate, and extraction with ether. The oil thus obtained soon solidifies over sulphuric acid, and on crystallisation from chloroform, is obtained in large, hard prisms, which melt at 91° and turn yellow in the air. The yield of amidotolylurethane is about 15 per cent. of the nitro-derivative employed. On boiling with alcohol and ethyl oxalate, it gives the urethanotolyloxamethane melting at 131°, described above, and so establishes the constitutions both of that substance and its isomeride melting at 128°.

Amidotolyloxamic acid, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OH$ $[Me : NH_2 : NH = 1 : 2 : 4]$, is formed during the preparation of amidotolyoxamethane if aqueous alcohol be used. The crude acid contains amidotolyloxamethane; this is eliminated by solution in alcoholic ammonia, when the oxamethane is converted into insoluble amidotolyloxamide, which

is filtered off. On treating the filtrate with acetic acid, amidotolyloxamic acid separates as a crystalline powder. It decomposes at 223°, and yields tolylenediamine and oxalate on boiling with solutions of alkali carbonates; when heated in a closed tube with alcoholic ammonia, a mixture of amidotolyloxamide, oxamide, and oxalic acid is obtained. It yields oxanilide and tolylenediamine on boiling with aniline. A small quantity of the acid is formed on prolonged boiling of an alcoholic solution of tolylenediamine (15 grams) and anhydrous oxalic acid (11 grams).

Amidotolyloxamide, $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot NH_2$, formed by the action of alcoholic ammonia on amidotolyloxamethane, crystallises from boiling alcohol in splendid scales which melt at 203°. It is also formed on heating a mixture of tolylenediamine and ethyl oxamate in molecular proportion for several hours at 110—115°.

Amidotolyloxanilide, $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot NHPh$, is prepared by boiling amidotolyloxamethane or its amide for a short time with aniline. It is also formed by fusing together phenyloxamethane and tolylenediamine. When crystallised from acetic acid, it melts at 185—186°; if crystallised from alcohol, at 183°. It yields a *hydrochloride* which loses about one-half its hydrogen chloride over sulphuric acid at the ordinary temperature. All the preceding compounds which contain one amido-group of the tolylenediamine intact give a red or violet colour with furfuraldehyde in presence of an acid.

Urethanotolyloxamic acid, $COOEt \cdot NH \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot OH$

$[Me : NH \cdot CO : NH \cdot C_2O_2 = 1 : 2 : 4]$,

is prepared by slowly adding ethyl chlorocarbonate (1 mol.) to finely-powdered potassium amidotolyloxamate (1 mol.) suspended in ether. The ether is distilled off, and the residue dissolved in dilute ammonia solution after extraction with acidified water. The acid is then precipitated by hydrochloric acid, and on crystallisation from alcohol is obtained in colourless scales, which are very soluble in alcohol, less so in ether, and only sparingly in water. It melts at 168—170°, and contains half a molecule of water of crystallisation, which it loses at 90—100°, but retains over sulphuric acid. The *silver* salt is a white, crystalline powder, and the *copper* salt a green, flocculent precipitate. If, in the preparation of the oxamethanotolylurethane melting at 128°, as described above, 90 per cent. alcohol is used, the mother liquors contain a substance of very sweet taste, which seems to be this urethanotolyloxamic acid. The analytical numbers obtained, however, differ much among themselves.

Uramidotolyloxamic acid, $NH_2 \cdot CO \cdot NH \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot OH$

$[Me : NH \cdot CO : NH \cdot C_2O_2 = 1 : 2 : 4]$,

is formed on adding the equivalent quantity of potassium cyanate solution to amidotolyloxamic acid suspended in ice-cold water. The new acid separates on adding hydrochloric acid to the solution, and when recrystallised from alcohol melts at 203°. It is insoluble in water, but readily dissolves in dilute alkalis and solutions of the alkali carbonates.

On mixing aqueous solutions of potassium cyanate and amidotolyloxamethane sulphate in molecular proportion, a crystalline separation

of *uramidotolyloxame'hane*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OEt$, is obtained. This, when washed with water and alcohol, yields colourless crystals which melt at 218°, and are sparingly soluble in alcohol and water. When this substance is heated in a closed tube at 80—100° with alcoholic ammonia, a partial conversion into *uramidotolyloxamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}NH_2$, occurs. This compound is, however, best prepared by the action of potassium cyanate solution on amidotolyloxamide sulphate. It melts at 239°, and is sparingly soluble in boiling alcohol.

Tolylenedioxamethane, $C_6H_3Me(NH{\cdot}C_2O_2{\cdot}OEt)_2$ [Me : NH : NH = 1 : 2 : 4], is formed on boiling a solution of amidotolyloxamethane in absolute alcohol with ethyl oxalate. It is found, as above mentioned, in the last mother liquors obtained in the preparation of amidotolyloxamethane, and may be conveniently extracted therefrom. These mother liquors are evaporated to dryness, and extracted with dilute hydrochloric acid to remove the tolylenediamine and amidotolyloxamethane. The residue is repeatedly extracted with ether, and on evaporating the ethereal solution, the substance is obtained in small needles melting at 130°. It is also formed in small quantity on heating amidotolyloxamethane with ethyl oxamate at 160°. It is very soluble in alcohol, but insoluble in hot water. Its alcoholic solution is fluorescent.

Oxamethanotolyloxamide, $EtO{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}NH_2$

[Me : EtO : NH_2 = 1 : 2 : 4],

can be prepared by boiling an alcoholic solution of amidotolyloxamide with ethyl oxalate. It crystallises from dilute alcohol in groups of colourless needles, and melts with decomposition at about 210°. It is also formed, together with other substances, on prolonged boiling of an alcoholic solution of amidotolyloxamide and ethyl oxamate.

Amidotolyloxamethane, $NH_2{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OEt$

[Me : NH_2 : OEt = 1 : 2 : 4],

an isomeride of the preceding compound, is prepared by directly heating together amidotolyloxamethane (4 grams) and ethyl oxamate (2·25 grams) at 160—170° for three hours. On cooling, the crystalline mass is dissolved in boiling alcohol, from which the pure substance separates in colourless, interlacing needles decomposing at about 200°. On heating it with dilute potash, it is decomposed with evolution of ammonia.

Tolylenedioxamide, $C_6H_3Me(NH{\cdot}C_2O_2{\cdot}NH_2)_2$ [Me : NH : NH = 1 : 2 : 4], may be prepared by the action of alcoholic ammonia on either of the three preceding compounds. It is a white powder, sparingly soluble in alcohol and insoluble in water and hydrochloric acid; it decomposes at about 220°. When heated for a short time with aniline, it evolves ammonia and alcohol vapour, and probably yields the corresponding dianilide; prolonged boiling causes the formation of oxanilide. In the preparation of tolylenedioxamide by the action of alcoholic ammonia on tolylenedioxamethane, a substance of intensely sweet taste is found in the last mother liquors. When these are evaporated, and the residue extracted with water, a solution is obtained which, on concentration over sulphuric acid, yields crystalline crusts

consisting probably of *tolylenedioxamic acid*, $C_6H_3Me(NH\cdot C_2O_2\cdot OH)_2$. The numbers obtained on analysis of the *silver*, *barium*, and *lead* salts, however, do not agree very well. These salts are crystalline, and sparingly soluble in water. They decompose slightly on washing with hot water, oxalate being formed. W. J. P.

Commercial Benzoic Chloride. By V. Meyer (*Ber.*, **24**, 4251).—Commercial benzoic chloride is generally contaminated with chlorobenzoic chloride, and the benzoyl compounds prepared with it, especially if the Schotten-Baumann method be employed, often contain chlorinated derivatives, which, by reason of their more sparing solubility than the simple benzoyl compounds, cannot be got rid of by crystallisation. The author instances a case of a benzoyl derivative which, after being several times recrystallised, was found to contain 1·5 per cent. of chlorine. A. R. L.

Benzoyl Compounds. By E. Hoffmann and V. Meyer (*Ber.*, **25**, 209—213).—Benzoic chloride frequently contains, in addition to chlorobenzoic chloride (compare preceding abstract), small quantities of benzaldehyde. The occurrence of the last-named compound is, perhaps, due to the fact that benzoic chloride is sometimes prepared commercially by treating benzotrichloride with lead or zinc oxide; commercial benzotrichloride contains a little benzal chloride, which, under these conditions, would be converted into benzaldehyde.

The presence of the benzaldehyde in benzoic chloride was discovered in studying the action of the chloride on very dilute ammonia; in addition to benzamide, the authors obtained a small quantity of benzylidenedibenzamide, $CHPh(NH\cdot COPh)_2$. F. S. K.

Oxidation Products of Paradibromohomocumic Acid. By M. Fileti and L. Boniscontro (*Gazzetta*, **21**, ii, 389—398).—By the oxidation of dibromohomocumic acid with potassium permanganate, Fileti and Basso (Abstr., 1891, 1057) obtained paradibromocumic and hydroxypropylparadibromobenzoic acids. The latter, when treated with hydrochloric acid, instead of giving rise to the unsaturated propenyldibromobenzoic acid, left a product undistinguishable from paradibromocumic acid. The authors have accordingly reinvestigated the subject.

Hydroxypropylparadibromobenzoic acid, $COOH\cdot C_6H_2Br_2\cdot CMe_2\cdot OH$ [$COOH : Br_2 : CMe_2\cdot OH = 1 : 2 : 5 : 4$]. Solutions of potassium permanganate (6·25 grams) in water (150 c.c.) and of dibromohomocumic acid (5 grams) in soda (150 c.c. of 4 per cent. solution) are gradually mixed, left on the water-bath for 12 hours, the excess of permanganate decomposed with a little alcohol, and the liquid concentrated and precipitated with hydrochloric acid in the cold. The precipitate consists of a mixture of dibromocumic and hydroxypropyldibromobenzoic acids, from which the latter may be dissolved out by boiling light petroleum. The other acid crystallises from a mixture of equal volumes of alcohol and water in prisms melting at 214—215°; it dissolves in alcohol, acetone, and methyl alcohol, sparingly in boiling chloroform and benzene, and not at all in water or light petroleum. The *barium* salt, $(C_{10}H_9Br_2O_3)_2Ba,2H_2O$, crystal-

lises in very soluble, lustrous prisms, becomes anhydrous at 100°, and at 150° loses a further quantity of water without blackening, and is partly converted into a salt of propenyldibromobenzoic acid. The *calcium* salt, with 3 mols. H_2O, crystallises in prisms, becomes anhydrous at 130°, and at 150° undergoes similar changes to the barium salt. The *magnesium* salt, with 5 mols. H_2O, crystallises in slender needles, which become anhydrous at 100°. The *acetyl* derivative [CMe_2·OAc = 4], prepared by the action of acetic chloride on the acid, crystallises from light petroleum in tufts of lustrous needles melting at 92°. It is decomposed by boiling with water, especially if acidified with acetic or hydrochloric acid.

Paradibromocumic acid, $C_6H_2PrBr_2$·COOH [COOH : Br_2 : Pr = 1 : 2 : 5 : 4], obtained in the preparation of the preceding compound, has already been described (Abstr., 1891, 1055). The *barium* salt, with 1 mol. H_2O, crystallises in long needles, which become anhydrous at 100°. The *calcium* salt forms tufts of microscopic crystals with 1 mol. H_2O; the *potassium* salt forms large, very soluble, tabular crystals; the *silver*, *lead*, and *copper* salts are insoluble. The *acid chloride* is a heavy liquid, decomposed by water; the *amide*, $C_{10}H_{11}Br_2ON$, crystallises from aqueous alcohol in needles melting at 191—192°, and is very soluble in alcohol, benzene, and chloroform, but only sparingly in light petroleum.

Parapropenylparadibromobenzoic acid, $C_6H_2Br_2Pr$,COOH, prepared by boiling hydroxypropyldibromobenzoic acid with hydrochloric acid [1 : 2] for three hours, crystallises in triclinic prisms resembling those of dibromocumic acid in appearance, and melting like them at 149°. It is very soluble in benzene, chloroform, ether, acetone, and acetic acid, but only very sparingly in boiling water. Contrary to what was stated previously, a solution of the acid in chloroform absorbs bromine at the ordinary temperature, no trace of hydrobromic acid being formed; the crude product melts between 120° and 140°. The *barium* salt crystallises in needles containing $2\frac{1}{2}$ mols. H_2O; the *calcium* salt forms acicular crystals with 3 mols. H_2O; both salts are more soluble in water than the corresponding dibromocumates. The *amide*, $C_{10}H_9Br_2ON$, crystallises in needles melting at 201—203°; it is very soluble in alcohol, benzene, and chloroform, but almost insoluble in light petroleum.

Mononitropropenyldibromobenzoic acid, NO_2·C_6HBr_2Pr·COOH, prepared by treating the preceding acid with a large excess of nitric acid (1·52), crystallises in needles, melts at 176—177°, dissolves readily in alcohol, ether, and acetone, and moderately in boiling water, but is almost insoluble in light petroleum. The corresponding derivative of dibromocumic acid melts at 199—200°.

S. B. A. A.

Paramethylhydratropic Acid. By G. Errera and G. Baldracco (*Gazzetta*, **21**, ii, 465—473).—Paramethylhydratropic acid and paramethylhydratropaldehyde, according to the constitution assigned to them by Miller and Rohde (Abstr., 1891, 898), and by Errera (Abstr., 1891, 1020), contain an asymmetrical carbon atom. The following attempts were made to split the acid and aldehyde into their active constituents.

A few grams of the acid and a little ammonia were added to a nutritive liquid containing 2·5 grams per litre of a mixture of potassium phosphate (50 parts), magnesium sulphate (48 parts), and calcium chloride (2 parts). The solution was then sown with *Penicillium glaucum* and left for a month at the ordinary temperature. Similar experiments were made with the aldehyde, acidifying the solution with a little phosphoric acid. No trace of vegetation was, however, observed in either case.

Negative results were also obtained from the following experiment. An alcoholic solution of quinine and paramethylhydratropic acid in molecular proportion, on evaporation, left a viscous oil which soon solidified. This, when fractionally crystallised from dilute alcohol, yielded beautiful, waxy needles, extremely soluble in alcohol, insoluble in water, and melting at 113—116°. The acid separated from different fractions of the salt never showed any deviation of polarised light.

Metadinitroparamethylhydratropic acid, $C_6H_2Me(NO_2)_2{\cdot}CHMe{\cdot}COOH$ [CH : $(NO_2)_2$: Me_2 = 1 : 2 : 6 : 4 or 1 : 3 : 5 : 4], is prepared by dissolving paramethylhydratropic acid in nitric acid (sp. gr. 1·52), cooled with water. On pouring the solution into water, the nitro-derivative separates as a flocculent precipitate or as an oil which immediately solidifies. The crude product is collected and dissolved in a little boiling benzene; hot petroleum (boiling at 80—110°) is now added until a permanent precipitate is almost formed. The nitro-derivative separates from this solution in large, straw-coloured, acicular crystals melting at 122—123°, and turning brown in the air. It is very soluble in benzene and alcohol, sparingly so in boiling water. When heated above its melting point, it deflagrates. Its *barium* salt, $(C_{10}H_9N_2O_6)_2Ba + 4H_2O$, is soluble in water and loses 2 mols. H_2O below 160°. The *methyl* salt is formed by saturating a solution of the acid in methyl alcohol with hydrogen chloride. It is a dense liquid which solidifies on cooling in a mixture of ice and salt.

Metadiamidoparamethylhydratropic acid is prepared by saturating an ammoniacal solution of the preceding acid with hydrogen sulphide. The solution thus obtained is heated, filtered from sulphur, and treated with dilute acetic acid, when the amido-acid separates as a grey, flocculent precipitate, very soluble in mineral acids and alkalis, sparingly so in the ordinary solvents.

Metadiamidoparamethylethylbenzene,

$C_6H_2MeEt(NH_2)_2$ [Et : $(NH_2)_2$: Me = 1 : 2 : 6 : 4 or 1 : 3 : 5 : 4],

is prepared by distilling the barium salt of the preceding acid with baryta. The oily liquid thus obtained soon solidifies and crystallises from water in colourless, rhombic laminæ, which turn slightly brown on exposure to light. It melts at 71—72°, boils at about 300°, and is very soluble in alcohol, sparingly so in water. Its aqueous solution is precipitated by alkalis. The *hydrochloride*, *sulphate*, and *oxalate* are very soluble in water. The base does not yield an insoluble phenanthrazine when boiled with phenanthraquinone and acetic acid in alcoholic solution, and is, therefore (Hinsberg, *Annalen*, **237**, 342), not an orthodiamine. On heating

the hydrochloride at 120° with ammonium thiocyanate, extracting with water, dissolving the residue in potash solution, and adding lead acetate, a precipitate of lead sulphide is obtained. This reaction is common to both meta- and para-diamines (Abstr., 1885, 976). The hydrochloride, however, evolves hydrogen chloride on heating at 100—120° with benzaldehyde. This is Ladenburg's reaction for orthodiamines (Abstr., 1878, 571), but has been shown by Lellmann (Abstr., 1885, 973) not to hold universally. On treating an aqueous solution of the base with diazobenzene nitrate, a yellow precipitate, which dissolves to a red solution on adding excess of acid, is obtained. This reaction shows that the base is a metamido-derivative, but the position of the amido-groups, with respect to the methyl group, could not be determined. W. J. P.

Action of Nitric Acid on Phenylglycollic Acid. By J. Pratesi (*Gazzetta*, **21**, ii, 402—404).—On nitrating phenylglycollic acid with fuming nitric acid (44° B.) in the ordinary way, a mixture of two nitro-derivatives may, contrary to Fritzsche's statement (*Jahresb. der Chem.*, 1879, 694), be separated with ease. By fractional crystallisation from alcohol and water, this is split up into paranitrophenylglycollic acid melting at 183° and a compound melting at 141—142°. The latter consists of a mixture of the orthonitro-acid melting at 156·5° and of the para-acid. This is shown by the identity of its reduction products with those of such a mixture, by the fractional crystallisation and decomposition of the mixed barium salts, and by acting on the mixture melting at 141—142° with potash, acidifying, and distilling, when orthonitrophenol passes over, and paranitrophenol remains in the residue. If the nitration is performed with nitric acid of 48° B., orthoparadinitrophenylglycollic acid is formed. S. B. A. A.

α-Methylphthalic Acid. By S. v. Niementowski (*Monatsh.*, **12**, 620—636).—The author has prepared homophthalonitrile according to Glock's method (Abstr., 1888, 1290), and finds that its melting point is 120°, that is, 3° higher than given by that author. On heating the nitrile (3 grams) with hydrochloric acid of sp. gr. 1·19 (16 grams) for three hours at 140° in sealed tubes, *α-methylphthalic acid* was obtained. The pure acid melts at 152°, is readily soluble in water, alcohol, ethyl acetate, and acetone, is dissolved sparingly by chloroform and benzene, but crystallises well from hot xylene. On dry distillation, it loses water, and is converted into the corresponding *anhydride*, $C_6H_3Me{:}C_2O_2{:}O$, which dissolves readily in most of the common organic solvents, crystallises in needles, melts at 92°, and, on heating with water, is reconverted into the acid.

α-Methylphthalimide, $C_6H_3Me{:}C_2O_2{:}NH$, is formed on heating a mixture of α-methylphthalic anhydride (2 mols.) and carbamide (1 mol.). It is soluble in boiling water and in acetone, crystallises from spirit in short needles, and melts at 196°.

α-Methylphthalodiamide, $C_6H_3Me(CONH_2)_2$, is obtained by the action of strong ammonia on α-methylorthophthalimide. It is readily solu-

ble in water, crystallises in needles, and melts at 188° with evolution of ammonia.

Paratolyl-α-methylphthalimide, $C_6H_3Me{:}C_2O_2{:}N{\cdot}C_6H_4Me$ [N : Me = 1 : 4], is formed on heating a mixture of α-methylorthophthalic acid with paratoluidine in molecular proportion. It is insoluble in water, dissolves readily in cold chloroform, benzene, and ethyl acetate, forms colourless crystals, and melts at 180°.

α-Methylhydroxyphthalanil, $C_6H_3Me{:}C_2O_2{:}N{\cdot}C_6H_4{\cdot}OH$ [N : OH = 1 : 3], is obtained by the action of orthoamidophenol on α-methyl orthophthalic anhydride in molecular proportion. It dissolves in alcohol, from which it crystallises in groups of colourless, six-sided scales, and melts at 205°.

α-Methylhydroxyphthalanilic acid, $COOH{\cdot}C_6H_3Me{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, is formed when the preceding compound is boiled with soda, and the filtered solution is acidified with hydrochloric acid. It is insoluble in water, dissolves in hot spirit, acetone, and solutions of the alkalis and of the alkali carbonates, crystallises in slender, white needles, and melts at 200°, with evolution of gas and formation of the corresponding anhydride. G. T. M.

Action of Ethyl Acetoacetate on Quinone: Synthesis of Benzofurfuran Derivatives. By M. Ikuta (*J. pr. Chem.* [2], **45**, 65—83).—When chloranil is treated with ethyl acetoacetate, one or two chlorine atoms are replaced by the acetoacetate group, and from the mono- and di-substitution products thus obtained, a number of furfuran derivatives can be synthesised.

Ethyl trichloroquinoneacetoacetate, $C_6Cl_3O_2{\cdot}C_6H_9O_3$, is obtained as follows:—Ethyl acetoacetate (10 grams) is dissolved in benzene (100 c.c.), and converted into the sodium compound by the addition of sodium wire: finely powdered chloranil (18 grams) is then gradually added to the emulsion with careful shaking. The mixture turns blue, then dark-green, and finally brown, and the reaction is completed by warming on the water-bath or by allowing the mixture to remain some hours in the cold. The product is filtered, the benzene distilled off, and the dark orange oil thus obtained, which consists of a mixture of ethyl acetoacetate and the mono- and di-acetoacetate derivatives of chloranil, is mixed with a little alcohol, and, on stirring it with a glass rod, is obtained crystalline. By crystallisation from alcohol, large, orange rhombohedra of ethyl dichloroquinonediacetoacetate are obtained, and can be easily separated mechanically. The red monacetoacetate is then recrystallised from alcohol until it melts at 14°. It is easily soluble in benzene, chloroform, and hot alcohol, more sparingly in acetic acid, and least so in ether. It dissolves in alkalis and ammonia with a blue coloration, which soon changes to orange-yellow; the alcoholic solution gives a blood-red coloration with ferric chloride. With aniline, it yields a colourless additive product, melting at 146°, and with fuming nitric acid a yellow, very unstable substance. By reducing agents, it is easily converted into the corresponding quinol.

Ethyl trichloroquinolacetoacetate, $C_6Cl_3(OH)_2{\cdot}C_6H_9O_3$, is obtained by adding zinc-dust and sulphuric acid in small quantities at a time to a

solution of the preceding compound in 6 parts of alcohol. The product is precipitated with water and crystallised from benzene. It forms colourless rhombohedra, melts at 132°, is sparingly soluble in most organic solvents in the cold, dissolves in alkalis with a pale-yellow colour, which soon changes to dark-green, and then to yellow, and easily loses the elements of water, being converted into a benzofurfuran derivative.

Ethyl trichloroparahydroxybenzofurfuran-α-methyl-β-carboxylate,

$$OH\cdot C_6Cl_3<\overset{\text{——O——}}{C(COOEt)}>CMe,$$

is obtained by boiling the above quinol derivative with 10 parts of acetic acid containing a few drops of concentrated sulphuric acid until it no longer gives a coloration with alcoholic ferric chloride. On dilution with a small quantity of water, it separates in colourless, transparent needles. It melts at 138°, is easily soluble in chloroform, less so in alcohol, ether, and cold acetic acid, gives no coloration with ferric chloride, yields a colourless solution in alkalis, and is easily hydrolysed by alcoholic potash. When warmed with concentrated sulphuric acid, it gives a dark, reddish-blue coloration. The author points out that Hantzsch's method of synthesis (*Ber.*, **19**, 1292, 2930, **20**, 1332) yields α-ethylcarboxylate-β-methyl derivatives, whilst the above synthesis yields α-methyl-β-ethylcarboxylate derivatives.

Trichloroparahydroxybenzofurfuran-α-methyl-β-carboxylic acid is obtained by heating the preceding ethyl salt with twice the calculated quantity of alcoholic potash. It crystallises from acetic acid in colourless, transparent needles, melts at 258°, distils without decomposition, and behaves like its ethyl salt towards organic solvents, concentrated sulphuric acid, and alkalis.

Ethyl paradichloroquinonediacetoacetate, $C_6Cl_2O_2(C_6H_9O_3)_2$, is prepared in the same way as the monacetoacetate, except that double the proportion of ethyl sodacetoacetate is used. It crystallises in pure yellow rhombohedra or in rhombic tablets, melts at 127—128°, is easily soluble in benzene and chloroform, less so in alcohol, acetic acid, and ether. In dilute alkalis, it dissolves with a deep bluish-violet coloration, which soon changes to brown. With sodium nitrite, it yields a compound which crystallises in yellow prisms, melts at 184°, and contains chlorine and nitrogen. Fuming nitric acid converts it into a very unstable yellow substance. With ferric chloride, it gives a deep blood-red coloration. It yields additive compounds with great ease.

Ethyl paradichloroquinoldiacetoacetate is obtained by reducing the preceding compound. It crystallises from benzene in transparent, colourless rhombohedra, melts at 154°, resembles ethyl trichloroquinolacetoacetate in its behaviour towards ferric chloride, alkalis, and solvents, and easily loses 2 mols. of water yielding a furfuran derivative.

Diethyl paradichlorobenzoparadifurfuran-α-dimethyl-β-dicarboxylate, $C_6Cl_2(<\overset{\text{——O——}}{C(COOEt)}>CMe)_2$, is obtained in theoretical quantity by boiling the preceding quinol derivative with acetic acid containing a

few drops of concentrated sulphuric acid. It crystallises from acetic acid in transparent needles, melts at 175°, is insoluble in alkalis, gives a deep bluish-green coloration with concentrated sulphuric acid, is sparingly soluble in most organic solvents with the exception of chloroform. and, when treated with chlorine in chloroform solution, yields a pale-yellow, oily additive product which is converted into the original substance by reduction with zinc-dust and acetic acid.

Paradichlorobenzoparadifurfuran-α-dimethyl-β-dicarboxylic acid is obtained by heating its diethyl salt with twice the theoretical quantity of alcoholic potash on the water-bath. On distilling off the alcohol and adding water, and then acetic acid, the acid is obtained as a white, crystalline powder consisting of microscopic needles It sublimes at high temperatures without melting, is quite insoluble in water and organic solvents, and gives a bluish-green solution with concentrated sulphuric acid.

Additive Products of Ethyl Paradichloroquinonediacetoacetate.—If the diacetoacetate is treated with bromine (1 mol.) in chloroform solution, the bromine is completely absorbed without the evolution of hydrogen bromide, and a colourless compound is obtained which crystallises in leaflets and melts at 216°. The author believes this compound to be a *dibromide* mixed with some tetrabromide. It is volatile without decomposition, and when treated with zinc-dust and acetic acid, or with zinc-dust and dilute sulphuric acid, yields diethyl dichlorobenzodifurfurandimethyldicarboxylate.

Diethyl quinoneparadifurfuran-α-dimethyl-β-dicarboxylate hydrochloride is obtained by warming ethyl dichloroquinonediacetoacetate with 3 parts of acetic acid (95 per cent.) containing a few drops of dilute sulphuric acid (1 : 5) until the orange solution has become nearly colourless. On diluting with water, it is obtained in oily drops which soon solidify. It crystallises from a mixture of chloroform and ether in stellate groups of leaflets or short prisms, melts at 171°, sublimes without decomposition, is easily soluble in organic solvents, insoluble in water and carbonates, and gives a deep-blue coloration when warmed with concentrated sulphuric acid. When heated with alcoholic potash, the *bibasic acid*, $C_{14}H_{10}Cl_2O_8$, is obtained. This crystallises from hot water in colourless needles, and decomposes at 220° with evolution of carbonic anhydride.

v. Pechmann (*Ber.*, **21**, 3005) has described a condensation product, obtained by the action of zinc chloride on a mixture of quinone and ethyl acetoacetate, which yields a bibasic acid on hydrolysis. He gives the formulæ $C_{16}H_{16}O_6$ and $C_{14}H_{12}O_6$ respectively for these compounds. The author has studied the above reaction, and finds that these compounds have the formulæ $C_{18}H_{18}O_6$ and $C_{14}H_{10}O_6$ respectively.

Ethyl benzoparadifurfuran-α-dimethyl-β-dicarboxylate,

$$C_6H_2(<\overset{\text{——}O\text{——}}{C(COOEt)}>CMe)_2,$$

is obtained by heating quinone (1 mol.) with alcohol and ethyl acetoacetate (2 mols.) in the presence of zinc chloride, as suggested by v. Pechmann, who has accurately described the properties of the

compound. The alcoholic mother liquors contain quinol and a new substance of the formula $C_{12}H_{12}O_4$. The above constitution is proved by the fact that, when treated with chlorine, the compound yields a dichlorinated compound which is identical with the diethyl para-dichlorobenzoparadifurfuran-α-dimethyl-β-dicarboxylate described above. When hydrolysed with alcoholic potash, it yields the corresponding dicarboxylic acid, $C_{14}H_{10}O_6$.

Ethyl parahydroxybenzofurfuran-α-methyl-β-carboxylate,

$$OH\cdot C_6H_3<\overset{\text{——O——}}{C(COOEt)}>CMe,$$

is contained in the alcoholic mother liquors from the preparation of the preceding compound. It is best obtained by treating quinone (1 mol.) and ethyl acetoacetate (1 mol.) in alcoholic solution with zinc chloride. The insoluble compound, $C_{18}H_{18}O_6$, is separated, and the filtrate allowed to evaporate spontaneously. It crystallises from petroleum (b. p. 70—80°) in colourless leaflets or flat needles, melts at 137°, is insoluble in water, soluble in alkalis, easily soluble in most organic solvents except light petroleum, and gives a purple-red coloration with concentrated sulphuric acid. E. C. R.

Trithioorthoformates. By E. Laves (*Ber.*, **25**, 347—360; compare Abstr., 1890, 988).—Phenyl trithioorthoformate is dissolved in benzene and treated with a mixture consisting of equal parts of 5 per cent. potassium permanganate solution and dilute sulphuric acid (2 per cent.); the liquid is well shaken and cooled, and the permanganate added in excess; the precipitated manganese dioxide is dissolved by sulphurous acid, and the sparingly soluble diphenylsulphonethiophenylmethane collected, dried, and purified by solution in chloroform and precipitation with ether. The properties of the compound have been previously described; on heating with soda and phenyl thiochloride, methyldiphenylsulphone and phenyl bisulphide are formed; with concentrated nitric acid, an oxidation product is obtained, which melts at 160° and contains nitrogen. The trisulphone, $CH(SO_2Ph)_3$, is formed by the oxidation of the disulphone sulphide with potassium permanganate in alkaline solution, and crystallises from alcohol or chloroform in colourless, rhombic plates. It has well-marked acid properties, and in aqueous solution reddens litmus paper and decomposes carbonates and acetates; it may be crystallised from concentrated sulphuric acid.

The *sodium salt* is readily soluble in water; the *potassium salt*, $CK(SO_2Ph)_3$, crystallises from dilute alcohol in small plates; the *silver salt* is obtained in long, thick, lustrous needles, which quickly decompose on exposure to light. The *barium* salt is deposited in rhombic plates.

Triphenylsulphonechloromethane, $CCl(SO_2Ph)_3$, is prepared by the action of chlorine on the sulphone in aqueous solution at ordinary temperatures; it is a colourless, amorphous, insoluble powder, melting at 260°; on heating with alcoholic soda, it decomposes into the trisulphone, benzenesulphonic acid, and carbonic anhydride.

The *bromo*-derivative, $CBr(SO_2Ph)_3$, is formed by the addition of bromine-water to a solution of the trisulphone; it melts at 255° with

decomposition, and resembles the chlorine compound in general properties, but is more unstable.

Triphenylsulphonemethylmethane, $CMe(SO_2Ph)_3$, may be obtained in small quantity by heating methyl iodide and alcoholic soda with triphenylsulphonemethane in a sealed tube at 115°, but is best prepared by the oxidation of phenyl trithioacetate (see below) with potassium permanganate in acid solution; it crystallises from alcohol in colourless, lustrous needles, melts at 182°, is insoluble in water or alkalis, and is not acted on by acids; with alkaline oxidising agents, benzenesulphonic acid and acetic acid are formed.

Trithiophenyl orthorthioacetate, $CMe(SPh)_3$, is obtained by the interaction of phenyl mercaptan (3 mols.) and ethenyl trichloride (2 mols.) in alkaline solution; it crystallises from alcohol in small, colourless, lustrous plates melting at 71·5°; the yield is quantitative. The compound gives a violet coloration with concentrated sulphuric acid, and is oxidised by nitric acid, but is not acted on by alkalis or dilute acids.

Triethyl orthothioacetate, $CMe(SEt)_3$, is prepared in a similar manner to the phenyl derivative by the mutual action of ethenyl trichloride, ethyl mercaptan, and soda, and is a brown, viscid liquid with an offensive smell; on oxidation, it yields the corresponding *trisulphone*, $CMe(SO_2Et)_3$, which crystallises in lustrous needles melting at 140°. On heating phenyl mercaptan with benzenyl trichloride and soda at 115° under pressure, a viscid liquid is obtained which, on oxidation, yields *benzylidenediphenylsulphone*, $CHPh(SO_2Ph)_2$, together with phenyl bisulphide and benzoic acid; the product is purified by extraction with soda and precipitation with carbonic anhydride, and crystallises from alcohol in small, colourless needles which melt at 262°; the same compound is also formed by the oxidation of phenyl mercaptan; it has feebly acid properties, is decomposed on heating with concentrated sulphuric acid, and does not yield haloïd substitution derivatives.

The product obtained from ethyl mercaptan, benzenyl trichloride and soda yields diethylsulphonephenylmethane, $CHPh(SO_2Et)_2$, on oxidation.

Benzyl trithioformate on oxidation yields a mixture of *dibenzylsulphonemethane*, $CH_2(SO_2C_7H_7)_2$, and *dibenzylsulphonethiobenzylmethane*, $C_7H_7{\cdot}S{\cdot}CH(SO_2C_7H_7)_2$, which may be separated by fractional crystallisation from chloroform; the former is readily soluble and is precipitated on the addition of ether as a colourless, amorphous powder which melts at 207·5°, dissolves readily in alcoholic soda, and is identical with the oxidation product of *methylene dibenzyl sulphide*, $CH_2(SC_7H_7)_2$. The disulphone sulphide is more sparingly soluble in chloroform, and crystallises from dilute acetic acid in small needles melting at 214°; it is not converted into a trisulphone by the action of alkaline permanganate.

Tribenzyl orthothioacetate, $CHMe(SC_7H_7)_3$, is formed by heating benzyl mercaptan (3 mols.) dissolved in soda (20 per cent.), with ethenyl trichloride (2 mols.) under pressure for five days at 115°; it is deposited from benzene at low temperatures in lustrous crystals which melt at 46°.

Benzylsulphonethiobenzylmethylmethane, $C_7H_7{\cdot}S{\cdot}CHMe{\cdot}SO_2{\cdot}C_7H_7$, is extracted from the oxidation product of the preceding compound by treatment with alcohol; it crystallises in colourless needles, melts at 151°, and is decomposed by sulphuric or nitric acid.

Tribenzylsulphonemethylmethane, $CMe(SO_2C_7H_7)_3$, is the chief compound obtained by the oxidation of the corresponding sulphide; it is sparingly soluble in alcohol, but readily dissolves in acetic acid, and crystallises from chloroform in slender needles melting at 218°.

The compound obtained from benzenyl trichloride and sodium benzylmercaptan could not be purified; on oxidation, *dibenzylsulphonephenylmethane*, $CHPh(SO_2C_7H_7)_2$, is formed, and is separated from the following compound by solution in alcoholic soda; it melts at 213°. *Tribenzylsulphonephenylmethane*, $CPh(SO_2C_7H_7)_3$, is readily soluble in chloroform, and crystallises in slender needles melting at 207°. The yield is very small. The above results show that the behaviour of trithioformates and trithioacetates towards oxidising agents is not identical; in presence of phenyl groups, the latter compounds yield trisulphone sulphides, whilst in presence of ethyl groups, disulphones are formed; in the case of the benzyl derivatives of trithioformic acid, disulphones and disulphone sulphides are formed, but benzyl trithioacetate yields a trisulphone together with bye-products different from those obtained by the oxidation of other trithioacetates.

J. B. T.

Formation of Trisulphones from Disulphones. By E. Laves (*Ber.*, **25**, 361—366).—*Diethylsulphonethiophenylmethylmethane*, $SPh{\cdot}CMe(SO_2Et)_2$, is prepared by heating diethylsulphonethiophenylmethane with methyl iodide and alcoholic soda in a sealed tube for two days at 90°; it crystallises from alcohol in colourless needles, melts at 113°, and is insoluble in alkalis at ordinary temperatures, and on heating yields acetic acid, sulphuric acid, ethylsulphonic acid, and phenyl bisulphide.

Diethylsulphonephenylsulphonemethane has previously been described by Fromm; it has well-marked acid properties, and decomposes carbonates and acetates; the *potassium salt*, $SO_2Ph{\cdot}CK(SO_2Et)_2$, crystallises from dilute alcohol in small prisms; the *barium salt* is deposited in rhombic plates.

Diethylsulphonephenylsulphonechloromethane, $SO_2Ph{\cdot}CCl(SO_2Et)_2$, is formed by the action of chlorine on the trisulphone in aqueous solution at the ordinary temperature; it crystallises from alcohol in small, lustrous plates melting at 130°.

The *bromo-derivative* is prepared in a similar manner to the preceding compound, which it closely resembles; it melts at 135°, crystallises from alcohol in lustrous scales, from water in slender needles, and from benzene in thick plates.

Diethylsulphonephenylsulphonemethylmethane, $SO_2Ph{\cdot}CMe(SO_2Et)_2$, could not be obtained from the preceding trisulphone, but is formed by the partial oxidation of diethylsulphonethiophenylmethylmethane, $SPh{\cdot}CMe(SO_2Et)_2$; it is purified by solution in chloroform and precipitation with ether, and crystallises from water in slender, white needles melting at 109°.

Attempts to introduce mercaptan or sulphone groups into the tri-

sulphone molecule were unsuccessful. Attempts to prepare a tetrasulphone by the action of sodium on haloïd trisulphones and of phenyl thiochloride on trisulphonates was also attended with negative results.

J. B. T.

Action of Methyl Iodide on α-Methylindole. By C. Zatti and A. Ferratini (*Gazzetta*, **21**, ii, 309—330; compare Abstr., 1891, 311).—It was shown by Ciamician and Zatti (Abstr., 1889, 1187), and by the authors (Abstr., 1890, 1292), that indole, on methylation, undergoes similar changes to pyrroline, the product being presumably a trimethyldihydroquinoline. The same product was also obtained from α- and β-methylindole and from αβ-dimethylindole (Abstr., 1889, 58, and 1890, 1431), but its constitution was not definitely ascertained.

The experiments which the authors made to prepare from the supposed trimethyldihydroquinoline a quinoline derivative of known composition were unsuccessful. On distilling the hydriodide with zinc powder, the principal product consists of trimethyltetrahydroquinoline; but above 300° an oily product of unknown composition passes over. On treating the base with sodium nitrite, a base of unknown composition is formed; this melts at 118° with decomposition, and may be converted into trimethyltetrahydroquinoline by reduction. Treatment with nitric acid gives rise to an amorphous, yellow substance which melts at 199—200°, and deflagrates when heated on platinum foil. By the action of an ethereal solution of bromine, the compound $C_{12}H_{15}NBr_2$ is obtained in tufts of large, yellow crystals which melt in a closed tube at 165—166°, but sublime and decompose at 172—173° in an open vessel. It is rapidly decomposed by warm water, but dissolves readily in the cold. The *platinochloride*, $(C_{12}H_{14}BrN)_2,H_2PtCl_6$, melts at 173—174°. *Trimethyldihydroquinoline* is unaffected by heating with hydrochloric or hydriodic acid at 180°, but a mixture of hydriodic acid and amorphous phosphorus converts it into a feebly basic compound which distils between 228° and 233°, and does not redden on exposure to the air. It yields a *nitrosamine* which gives Liebermann's reaction, and by the action of reducing agents is converted into a *dimethyltetrahydroquinoline*, $C_9NH_9Me_2$. This distils between 232° and 242° under a pressure of 758 mm., and forms an unstable *platinochloride*, which begins to decompose at 160° and melts at 192—195°. By the action of hydriodic acid and phosphorus, trimethyldihydroquinoline, therefore, loses the methyl group attached to the nitrogen, and is converted into a secondary base containing dimethyltetrahydroquinoline. On heating the latter with methyl iodide, trimethyltetrahydroquinoline methiodide is formed, together with small quantities of a product melting at 209°.

Dihydrotrimethylindole methiodide, $C_6H_4<\begin{matrix}CHMe\\NMe_2I\end{matrix}>CHMe$, prepared from dihydro-αβ-dimethylindole for comparison with the preceding bye-product, forms a white, crystalline mass, very soluble in alcohol, and melts with decomposition at 167—168° in a closed vessel, and at 170—171° in an open tube.

As no known quinoline derivative was isolated in the above experiments, an attempt was made to establish that the reduction product

of trimethyldihydroquinoline had the properties of a tetrahydroquinoline by comparing the reactions of the two compounds. No colouring matter is formed by trimethyldihydroquinoline, either on treatment with diazobenzene chloride or with zinc chloride, benzaldehyde, and ferric chloride; in the latter case, the yellow compound described by Fischer and Steche (Abstr., 1888, 298) may be isolated. On treating trimethyltetrahydroquinoline with amyl nitrite according to Baeyer and Caro's method, the *nitroso*-derivative, $NO{\cdot}C_9NH_7Me_3$, is formed; the corresponding *picrate* crystallises in shining, brownish-green scales which melt at 141—142° with decomposition. With zinc chloride, benzaldehyde, and ferric chloride, it yields an intensely green compound with a blue metallic reflex. With diazobenzene chloride, a compound is obtained of a deep violet colour with a metallic reflex; the *hydrochloride* of the azo-base forms large, deliquescent, violet crystals; the *picrate* crystallises in reddish-violet, rhomboïdal tables, which commence to decompose at 158°, and melt at 170°. The authors are of opinion that the analogies between the reactions of trimethyltetrahydroquinoline and the substituted aniline compounds, with sodium nitrite, diazobenzene chloride, and benzaldehyde sufficiently prove that the base is a tetrahydrogenated quinoline.

Pentamethyldihydroquinoline hydriodide, $C_{14}H_{20}NI$, prepared by heating trimethyldihydroquinoline with methyl iodide and previously described by the authors, melts at 173° with decomposition. The base is a light oil which reddens on exposure to the air and boils at 270° under a pressure of 762 mm. It forms no colouring matter with diazobenzene chloride or benzaldehyde. On heating its hydrochloric acid solution with picric acid, a yellowish, uncrystallisable oil is formed; a hydrochloric acid solution of ferric chloride produces an orange-yellow crystalline precipitate closely resembling that obtained from trimethyldihydroquinoline. It yields an unstable *aurochloride* and *platinochloride*.

Pentamethyltetrahydroquinoline, $C_9NH_6Me_5$, is obtained by reducing the hydriodide of the preceding base with tin and hydrochloric acid. It is a colourless, oily liquid which is unaffected by exposure to the air, and boils at 253—254° under a pressure of 759 mm. The *picrate* crystallises from alcohol in yellow scales which melt at 132—133°. With diazobenzene chloride, &c., the base behaves like tetrahydroquinoline and its trimethyl derivative.

On heating pentamethyldihydroquinoline with excess of methyl iodide, a methiodide, $C_6H_4{\cdot}C_3NMe_5{\cdot}MeI$ is formed, which melts with decomposition at 174—175°. It is hydrolysed by potash with the formation of a new base. The latter may be distilled in a current of steam, and forms a heavy, semi-solid mass which is not reddened by the air and is feebly alkaline to litmus paper. It is insoluble in water, but dissolves in ether and readily in acids forming the salts corresponding with the methiodide. The *platinochloride*, $(C_{15}H_{21}N)_2{\cdot}H\,PtCl_6$, crystallises in tufts of yellow needles, and melts at 175—176°; the *aurochloride*, $C_{15}H_{21}N{,}HAuCl_4$, forms yellow needles melting at 144—145°. This base, which may be regarded as the oxide or hydroxide of a quaternary ammonium, differs from the other non-hydrogenated alkaloïds derived from the indoles in its marked basic properties

and its indifference to the action of the air. On heating it with gaseous hydriodic acid, the methiodide is not re-formed, the product melting at 183°. It appears to be incapable of further methylation, as, on heating with methyl iodide, pentamethyldihydroquinoline methiodide is reproduced. S. B. A. A.

Carbazole. By G. Mazzara and A. Leonardi (*Gazzetta*, **21**, ii, 380—388).—It has been previously shown (Abstr., 1891, 570) that on treating benzoylcarbazole with fuming nitric acid, a mononitrobenzoylcarbazole is formed, which, on hydrolysis by treatment with potash, yields a mononitrocarbazole melting at 209°.

Amidocarbazole, $NH<^{C_6H_4}_{C_6H_3\cdot NH_2}$, prepared by reducing the nitro-compound with tin and hydrochloric acid, when pure crystallises from alcohol in tufts of minute, rose-coloured scales, which turn reddish-brown on exposure to the air. From chloroform, it separates in thin, transparent, colourless plates; it is only sparingly soluble in ether, and moderately in chloroform, but freely so in acetic acid or benzene. When heated in a capillary tube, it turns brown at 220°, and decomposes at 240—245°. When heated rapidly, it becomes discoloured at 235°, and melts at 246—248° with decomposition. With tin chloride, the hydrochloride yields the *salt*, $(C_{12}H_{11}N_2)_2,H_2SnCl_6$, which crystallises in yellowish-white, lustrous scales The *platinochloride*, $(C_{12}H_{11}N_2)_2,H_2PtCl_6$, is a brownish-green powder which is decomposed on washing.

Benzilidenamidocarbazole, $NH<^{C_6H_4}_{C_6H_3\cdot N:CHPh}$, is prepared by heating amidocarbazole with benzaldehyde at 120—140°; the product, when pure, crystallises from alcohol in somewhat greenish-yellow, lustrous scales, and from light petroleum in clear, yellow needles, melts at 209—210°, dissolves freely in benzene and moderately in ether. On boiling it with dilute hydrochloric acid, it is easily decomposed into benzaldehyde and amidocarbazole hydrochloride.

Benzoylamidocarbazole, $NH<^{C_6H_4}_{C_6H_3\cdot NHBz}$, is prepared by heating amidocarbazole and benzoic anhydride in molecular proportions at 160—200°. After purification by precipitating the alcoholic solution with dilute potash, and by repeated crystallisation from alcohol and concentrated acetic acid, it crystallises in leaden-grey plates with a metallic lustre, and melts at 250—251°.

Acetylamidocarbazole, $NH<^{C_6H_4}_{C_6H_3\cdot NHAc}$, is prepared by heating together amidocarbazole with acetic anhydride in molecular proportion. When pure, it crystallises in translucent, white plates, with a pale, pinkish tinge, melts at 213—214°, and dissolves very readily in concentrated acetic acid. It is not affected by prolonged boiling with methyl iodide.

Acetylamidonitrosocarbazole, $NO\cdot N<^{C_6H_4}_{C_6H_3\cdot NHAc}$, prepared by

treating an acetic acid solution of the preceding compound with potassium nitrite, separates from alcohol as a yellowish, crystalline powder, and melts with decomposition at 162—164°. It dissolves in concentrated acetic acid, and sparingly in benzene and light petroleum. It also dissolves in concentrated sulphuric acid, forming a bright-green solution. On heating it with an aqueous solution of stannous chloride, the acetamido-derivative is re-formed. The formation of the nitroso-derivative shows that the acetyl group is connected with the amido-group in these compounds. From the above experiments, it further appears that the amido-group in these compounds is not in the ortho-position with regard to the imido-group.

On treating a glacial acetic acid solution of amidocarbazole with a well-cooled solution of diazobenzene chloride, the product, after purification, crystallises from light petroleum in minute, pale-yellow prisms, and melts at 228—230°. It is very soluble in chloroform and benzene, but only sparingly in ether and light petroleum. It probably has the constitution of diazobenzeneamidocarbazole,

$$NH<\begin{matrix}C_6H_4\\ |\\ C_6H_3\cdot NH\cdot N_2Ph\end{matrix}$$

S. B. A. A.

Carbazacridines. III. Dehydration of Amides in contact with Diphenyl Derivatives. By D. Bizzari (*Gazzetta*, **21**, ii, 351—359).—The analogy between diphenylene oxide and carbazole rendered it probable that if diphenylene oxide were an ortho-derivative, the substitution of amidogen or an amido-group for oxygen would result in the formation of a carbazole derivative, which might be converted by dehydration into a carbazacridine derivative. When, however, acetamide and diphenylene oxide are heated with excess of phosphoric anhydride and zinc chloride, the diphenylene oxide remains in great part unaltered, only small quantities of resinous products being formed.

On heating carbazole (8 grams), acetamide (4 grams), and dry phosphoric anhydride (7 grams) at 150—160°, the products consist of methylcarbazacridine, together with unaltered carbazole, resinous products, and traces of ethyl acetate. When carbazole is heated with benzamide and phosphoric anhydride at 150°, phenolcarbazacridine is formed together with a little benzonitrile. The formation of the carbazacridines may be supposed to occur in two stages, the first product being an asymmetric amidine of the type NH:CR′·N:R″, which subsequently loses ammonia, thus

$$NH{:}CPh\cdot N<\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix} - NH_3 = \begin{matrix}C_6H_5\cdot C\!-\!C_6H_3\\ |\quad\quad |\\ N\!-\!C_6H_3\end{matrix}.$$

That amidines of the above composition are formed under these conditions may be shown by heating diphenylamine, acetamide, and dry phosphoric anhydride at 150° for 10 hours, when among the products a compound occurs which melts at 64°, and has approximately the properties of Bernthsen's ethenylisodiphenylamidine (Abstr., 1878, 788). Similarly, benzenylisodiphenylamidine is formed on heating benzamide, diphenylamine, and phosphoric anhydride for 21 hours at 170—180°. It is improbable that the formation of the

carbazacridines is due to the action of carbazole on the acids liberated from amides by phosphoric anhydride, as under the circumstances mere traces of acid are formed, which would be without influence on the result. S. B. A. A.

Paradiamidodiphenylmethane. By J. Gram (*Ber.*, **25**, 302—304).—Paradiamidodiphenylmethane (m. p. 85°) is now prepared by heating anhydroformaldehydeaniline with aniline and aniline hydrochloride (D.R.-P. 53,937), and is employed in the production of pararosaniline and rosaniline, which are formed when it is heated with aniline or 1 : 2-amidotoluene in the presence of an oxidising agent. The diacetyl derivative agrees with Staedel and Haase's description (Abstr., 1883, 990); whilst the *dibenzylidene* derivative, $C_{27}H_{22}N_2$, prepared by adding benzaldehyde to an alcoholic solution of the base, melts at 125. A *dinitro*-derivative, $C_{17}H_{16}N_4O_6$, is obtained when the acetyl derivative is dropped into nitric acid, sp. gr. 1·48 (5 parts); it forms lemon-yellow needles, melts above 300°, and is sparingly soluble in alcohol and benzene, less so in ether and water, readily soluble in phenol, and somewhat sparingly in glacial acetic acid. It is hydrolysed when heated with aqueous potassium hydroxide and a little alcohol, with the formation of *metadinitroparadiamidodiphenylmethane*, which crystallises from a mixture of phenol and alcohol in small, red needles, and melts at 224°; its reduction product yields azines with orthodiketones. *Orthodinitroparadiamidodiphenylmethane* is produced by nitrating paradiamidodiphenylmethane, dissolved in a large quantity of concentrated sulphuric acid, with potassium nitrate (2 mols.); the compound is precipitated by ammonia, dissolved in boiling dilute hydrochloric acid, reprecipitated by ammonia, and crystallised from dilute alcohol, being thereby obtained in lustrous, golden leaflets, melting at 202°; the *hydrochloride* crystallises in colourless needles, and is partially dissociated on heating at 100°, and also by the presence of a large excess of water. The research is being continued.

A. R. L.

Dicyanostilbene. By L. Chalanay and E. Knoevenagel (*Ber.*, **25**, 285—288).—In view of the fact that bidesyl and isobidesyl can be obtained from deoxybenzoïn (Knoevenagel, Abstr., 1888, 706), it seemed of interest to ascertain whether benzyl cyanide could in an analogous manner be converted into diphenylsuccinonitrile.

When benzyl cyanide (1 mol.) is added to a solution of sodium (1 equivalent) in alcohol (10 parts), the whole diluted with an equal volume of ether, and iodine (1 equivalent) dissolved in ether slowly dropped into the cooled liquid with shaking, a small quantity of dicyanostilbene, melting at 158° (Reimer, *Ber.*, **14**, 1797), is obtained from the resinous product, together with unaltered benzyl cyanide amounting to about half that employed. The mechanism of this reaction appears to be that a small quantity of diphenylsuccinonitrile is initially produced, and this, reacting with the sodium ethoxide, is converted into the sodium derivative, CN·CNaPh·CNaPh·CN, which is then converted into dicyanostilbene by the action of the iodine, with the elimination of 2 atoms of sodium (compare next abstract). It has, indeed, been experimentally proved that diphenylsuccino-

nitrile yields a small quantity of dicyanostilbene when it is suspended in sodium ethoxide and an ethereal solution of iodine added. The yield is augmented by increasing the quantity of sodium ethoxide and iodine, but is at most only 10—20 per cent. of the theoretical. When an ethereal solution of iodine (2 equivalents) is added to benzyl cyanide (1 mol.) in alcohol, and a solution of sodium (2 equivalents) slowly dropped in with cooling and shaking, 70—90 per cent. of the theoretical quantity of dicyanostilbene is produced with scarcely any resinous products. Dicyanostilbene is also readily formed from diphenylsuccinonitrile when the reagents are added in the last-mentioned order. It exhibits all the reactions and properties described by Reimer (*loc. cit.*), and when heated with a solution of potassium hydroxide in dilute alcohol, yields diphenylmaleïc anhydride (m. p. 150) on acidification.

A. R. L.

Stereoisomeric Diphenylsuccinonitriles. By L. Chalanay and E. Knoevenagel (*Ber.*, **25**, 289—301).—*Symmetrical dimethyldiphenylsuccinonitrile*, CN·CMePh·CMePh·CN, is obtained when methylbenzyl cyanide (hydratroponitrile) (1 mol.), prepared by V. Meyer's method (Abstr., 1889, 596), is added to a solution of sodium (1 equivalent) in methyl alcohol (10 parts), and iodine (1 equivalent) in ethereal solution slowly dropped in with agitation. The mixture is poured into water, and the precipitated compound crystallised from boiling alcohol; it is insoluble in benzene, only sparingly soluble in cold glacial acetic acid or alcohol, and melts at 227°. As the yield is small, the existence of isomerides could not be determined.

Symmetrical dibenzyldiphenylsuccinonitrile,

$$CN\cdot CPh(CH_2Ph)\cdot CPh(CH_2Ph)\cdot CN,$$

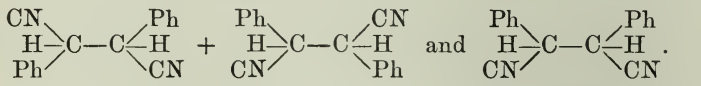
is prepared from benzylbenzyl cyanide in a manner similar to the last-described nitrile; it forms a white, crystalline powder, is insoluble in ether and benzene, sparingly soluble in alcohol, and melts at 235°. The compound is still under investigation.

Diphenylsuccinonitrile, CN·CHPh·CHPh·CN (dibenzylene dicyanide; Reimer, Abstr., 1882, 170), is obtained in considerable quantity when benzyl chloride and benzal chloride (1 mol. of each) are heated with potassium cyanide (3 mols.); also in yield amounting to 50—60 per cent. of the theoretical, when benzyl cyanide and benzal chloride (1 mol. of each) are heated in aqueous alcoholic solution in a reflux apparatus with potassium cyanide (2 mols.). By the action of benzaldehyde and potassium cyanide in alcoholic solution on benzyl chloride, the authors obtained a certain quantity of diphenylsuccinonitrile, together with benzoïn, α-phenylcinnamonitrile, and a nitrogenous compound melting at 180—181°, and after a study of the reaction, from a theoretical aspect, they discovered that diphenylsuccinonitrile is obtained in about 50 per cent. yield when mandelonitrile and benzyl cyanide (equal molecules) are heated with alcoholic potassium cyanide at 50—60° for 12—18 hours. The product crystallised from glacial acetic acid generally melts at 220—221°, but its melting point is very variable; it gives the dicarboxylic acid (β-dibenzyldicarboxylic acid, m. p. 229—230°; Reimer, Abstr., 1882, 200) when heated with concentrated hydrochloric acid at 150—160°.

When the nitrile as thus obtained is boiled with absolute alcohol for 12—18 hours in a reflux apparatus, the greater portion remains undissolved, and melts at 239—240° (β-modification); whilst a lower melting product separates from the alcoholic solution, and still lower ones on concentrating it; on evaporating the last alcoholic mother liquors to a small volume, a compound melting at 160° (α-modification) is obtained.

β-Diphenylsuccinonitrile, which represents the chief portion of the last-described crude product, is obtained as above mentioned; or the crude product (m. p. 220—221°) is boiled for several hours with glacial acetic acid, whereby the α-modification, which it contains, is converted into the β-modification; it crystallises from glacial acetic acid in colourless needles, melts at 239—240°, and is soluble in hot alcohol, and almost insoluble in the cold liquid, as also in ether, benzene, and chloroform. When heated with concentrated hydrochloric acid at 150—160° for 2—3 hours, it gives β-diphenylsuccinic acid (m. p. 229—230°; *loc. cit.*); on heating with alcohol at 180°, it decomposes into α-phenylcinnamonitrile (m. p. 84°) and hydrogen cyanide; whilst when heated with acetic acid and water at 160°, a compound, $C_{16}H_{13}NO_2$, having basic properties, is obtained.

α-Diphenylsuccinonitrile is obtained from the crude product as above described, but its isolation presents some difficulty; it melts at 160°, but agrees in other respects with the β-modification. When heated with concentrated hydrochloric acid at 150—160°, it yields the same diphenylsuccinic acid (m. p. 229—230°) as the β-modification, a result which is not surprising, in view of Reimer's observation that α-dibenzyldicarboxylic acid (m. p. 183°) is converted by heating it with concentrated hydrochloric acid into the β-modification (m. p. 229°). Both the diphenylsuccinonitriles are optically inactive, and the authors, regarding the α- and β-modifications as the analogues of racemic and mesotartaric acids respectively, propose the following spacial configurations for them:—



α-Diphenylsuccinonitrile. β-Diphenylsuccinonitrile.

A. R. L.

Metanitro- and Paranitro-diparadihydroxytriphenylmethane. By G. Bertoni and M. Zenoni (*Gazzetta*, **21**, ii, 331—336).—The authors have continued their experiments on the formation of nitrohydroxy-derivatives of triphenylmethane by Baeyer's reaction (compare Abstr., 1891, 1378, and *Rend. R. Ist. Lomb.*, **23**).

Metanitrodiparadihydroxytriphenylmethane,

$$NO_2{\cdot}C_6H_4{\cdot}CH[C_6H_3(OH)_2]_2,$$

is prepared by melting quinol (4·4 grams) with metanitrobenzaldehyde (3 grams) and treating the mixture with a little dilute sulphuric acid. The product, when pure, is a light, amorphous substance of a pink colour; it darkens at 250°, and begins to alter at 264°. It dissolves freely in alcohol, but is insoluble in cold water. In other

respects it resembles the nitrohydroxy-compounds previously described by the authors.

The *paranitro*-derivative is formed in a manner analogous to the preceding compound. It is a dull-white, uncrystallisable powder, insoluble in water, chloroform, or light petroleum, but very readily soluble in alcohol and ether. It turns brown at 260°, intumesces at 274°, and decomposes. When rapidly heated on platinum-foil or in a test tube, it evolves violet vapours. S. B. A. A.

Condensation Products of Nitrobenzaldehydes with Hydroxybenzenes. By G. Siboni (*Gazzetta*, **21**, ii, 340—345).—*Paranitrophenyldimetadihydroxyphenylmethane*,

$$NO_2{\cdot}C_6H_4{\cdot}CH[C_6H_3(OH)_2]_2.$$

—Resorcinol (7 grams) and paranitrobenzaldehyde (4 grams) are melted together and treated with dilute sulphuric acid; the product, after purification, is a clear, brick-red, uncrystallisable compound, soluble in ether, alkalis, &c., but not in water.

Orthonitrophenyldiparadihydroxyphenylmethane is prepared, like the preceding compound, from quinol (3·3 grams) and orthonitrobenzaldehyde (2·2 grams). It is a brown powder, resembling in properties the other nitrohydroxy-derivatives.

Metanitrophenyldiorthocresolmethane, $NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Me{\cdot}OH)_2$, prepared by the action of dilute sulphuric acid on orthocresol and metanitrobenzaldehyde, is a cinnamon-coloured powder. It dissolves in alcohol, forming brown solutions, which are turned violet by alkalis; acids precipitate it as a purplish-red, flocculent powder.

S. B. A. A.

Condensation of Nitrobenzaldehydes with Salicylic Acid. By G. de Varda (*Gazzetta*, **21**, ii, 345—350; compare Abstr., 1891, 1346).—*Metanitrophenyldihydroxyphenylmethanedicarboxylic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}CH[C_6H_3(OH){\cdot}COOH]_2,$$

is prepared by the action of concentrated sulphuric acid on a mixture of metanitrobenzaldehyde and salicylic acid. The pure product is a yellowish, amorphous substance, almost without odour or taste; it turns brown at about 200°, and partially fuses and turns black at 210—220°. It is moderately soluble in ether, alcohol, and acetic acid, and sparingly in benzene, chloroform, or boiling water; in the latter it becomes emulsified, and is slowly deposited as a pale-yellowish powder. It forms salts with the hydroxides of potassium, sodium, and barium, and is reprecipitated unchanged by acids from aqueous solutions of these salts. It is slightly soluble in hot concentrated sulphuric acid, which colours it reddish-brown.

The corresponding *ortho*-compound, formed from orthonitrobenzaldehyde, salicylic acid, and sulphuric acid, is a coffee-coloured, amorphous substance, without taste or odour; it darkens at 214—216°, swells up, and fuses. It is sparingly soluble in hot water, and becomes emulsified on cooling the solution; it is soluble in acetic acid, and partially in alcohol and ether. With alkalis, sulphuric acid, &c., it behaves like the meta-derivative. The *para*-compound is

an amorphous, dark-red substance, which turns brown at 200°, and softens at 215°. Its properties are in general very similar to those of the preceding compounds. None of these derivatives can be distilled or volatilised, and they only burn with difficulty.

S. B. A. A.

Metanitrophenylsantoninmethane. By G. Bertoni (*Gazzetta*, **21**, ii, 336—340).—*Metanitrophenylsantoninmethane*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C_{15}H_{16}O_3,$$

is prepared by melting metanitrobenzaldehyde (3 grams) with santonin (9·84 grams) and adding a few drops of hot dilute sulphuric acid to the molten mass. When pure, the product is a flocculent, uncrystallisable, orange-coloured substance, soluble in alcohol, acetic acid, &c., but almost insoluble in water. It softens at 107°, becomes transparent at 120°, and melts at 138°, simultaneously turning brown.

S. B. A. A.

Decomposition of Diazo-compounds of Nitronaphthalenes with Alcohol. By W. R. Orndorff and M. Cauffmann (*Amer. Chem. J.*, **14**, 45—57).—It was shown previously, that when a diazonaphthalene sulphate is decomposed by alcohol, two reactions occur, resulting respectively in the formation of naphthalene and of a naphthyl ethyl ether (Abstr., 1891, 1073); it is now found that in the case of the three diazonitronaphthalene sulphates, $NO_2{\cdot}C_{10}H_6{\cdot}N_2HSO_4$ [$NO_2 : N_2HSO_4 = 3 : 4$, $= 4 : 3$, and $= 1 : 4$, respectively; in the last case the nitrate was actually used], only the first reaction takes place, no ether being formed; the yield of nitronaphthalene is, respectively, 84, 52, and 57 per cent. of the theoretical.

3 : 4-*Nitrodiazonaphthalene sulphate* was obtained by dissolving the corresponding nitronaphthylamine in a little ordinary alcohol, adding gradually excess of concentrated sulphuric acid, cooling, adding rather more than the theoretical quantity of amyl nitrite, then adding ether, and again cooling. It forms yellow, monoclinic (?) prisms with a hexagonal section, and dissolves in water and dilute alcohol, but not in ether and absolute alcohol. It explodes when heated, but not on percussion. It decomposes when exposed to air and light, becoming red, and when boiled with water yields nitrogen and 3 : 4-nitronaphthol.

4 : 3-*Nitrodiazonaphthalene sulphate* was prepared in the same way as the 3 : 4-isomeride. It forms orange-yellow needles, which dissolve readily in water and dilute alcohol, sparingly in absolute alcohol, and not all in ether. It explodes feebly at 167°, but not when struck. It decomposes when exposed to air and light, turning brown; and when boiled with water yields nitrogen and 4 : 3-nitronaphthol. 4 : 3-*Nitrodiazonaphthalene nitrate* was prepared in the same way as the sulphate, concentrated nitric acid being used instead of sulphuric acid. It forms pale yellow needles, soluble in water and alcohol, insoluble in dry ether. It explodes when heated, but not when struck. It decomposes when exposed to light, turning dark-brown; and when boiled with water yields the same products as the sulphate.

1 : 4-*Nitrodiazonaphthalene nitrate* was prepared in a similar manner to the last-mentioned nitrate. It forms pale yellow needles, which

dissolve readily in water, moderately in alcohol, not at all in dry ether. It explodes feebly when heated, but not when struck. It decomposes when exposed to light, turning greenish-yellow.

In conclusion, the author advances the view that the formation of an ether by the action of alcohol on a diazo-compound never takes place when a nitro-group is present. The only exception, and that but a partial one, is the diazo-derivative of nitrotoluylenediamine.

C. F. B.

Tautomerism of Sulphinic Acids. By R. Otto and A. Rössing (*Ber.*, **25**, 230—233).—*Methyl β-naphthylsulphinate*, $C_{10}H_7 \cdot SOOMe$, can be easily prepared by treating sodium β-naphthalenesulphinate with methyl chlorocarbonate in ice-cold alcoholic solution; after adding water, the solution is extracted with water, and the extract evaporated, when there remains a mixture of methyl β-naphthylsulphinate and a substance melting at 92—93°, probably methyl naphthylsulphone formate, $C_{10}H_7 \cdot SO_2 \cdot COOMe$, which can be separated by treatment with light petroleum, in which the former alone is soluble. On evaporating the light petroleum solution at the ordinary temperature, methyl β-naphthylsulphinate is deposited in prismatic crystals melting at 44°, and readily soluble in ether, chloroform, alcohol, and ethyl acetate, but insoluble in water. It is readily hydrolysed by warm concentrated potash, and is also decomposed by boiling water; on oxidation with potassium permanganate, it gives a crystalline compound melting at 53—54°, which is probably methyl β-naphthylsulphonate.

β-Naphthylmethylsulphone, prepared from sodium β-naphthylsulphinate and methyl iodide, crystallises in lustrous, rectangular plates, melts at 139—140°, and is insoluble in water, but readily soluble in hot alcohol and benzene; it is not acted on by potash or by potassium permanganate.

In the first part of the paper, the authors reply to some criticisms of Baumann, who has questioned the existence of tautomeric sulphinic acids.

F. S. K.

Picene. By R. Lespieau (*Bull. Soc. Chim.* [3], **6**, 238—239).—Among the products of the action of ethylene bromide on naphthalene in presence of aluminium chloride, Roux noticed a hydrocarbon boiling above 450°, and crystallising as scales which melt about 300°. The author finds it very difficult to free this product from dinaphthyl and naphthalene hydrides, but finally obtained it in a state of sufficient purity to identify it with the picene, $C_{22}H_{14}$, described by Burg. The author failed to obtain the hydrocarbon by substituting acetylene bromide for ethylene bromide in the generating reactions.

T. G. N.

Terpenes and their Derivatives. By J. W. Brühl, H. Biltz, A. Cantzler, and L. Reuter (*Ber.*, **25**, 142—151; see also this vol., pp. 200, 347).—Menthene, which stands in the same relation to menthone as camphene to camphor, may be readily obtained by the action of dehydrating agents on menthol, phosphoric anhydride acting at the ordinary temperature, and zinc chloride at the boiling point. Concentrated sulphuric acid, on the other hand, even in the cold,

gives very little menthene, the chief product having a much higher boiling point. Anhydrous copper sulphate may also be employed with good results. To purify the menthene, it is heated with sodium on an oil-bath, and distilled over the metal in a vacuum; it boils at 167·1° under a pressure of 768·6 mm., and when heated with anhydrous copper sulphate at 250°, is converted into cymene. As menthol so readily loses water, the reaction probably takes place between the hydroxyl group and the hydrogen atom in the ortho-position, the constitution of menthol and menthene being represented by the following formulæ:—

$$CHPr^{\beta}<\begin{matrix}CH_2\cdot CH(OH)\\ CH_2\text{——}CH_2\end{matrix}>CHMe \text{ and } CHPr^{\beta}<\begin{matrix}CH:CH\\ CH_2\cdot CH_2\end{matrix}>CHMe.$$

Terebenthene was prepared from French oil of turpentine by shaking it with soda solution, drying over solid soda, and heating in an oil-bath with sodium until the surface of the latter remained bright. The product was then distilled, and two fractions collected boiling at 155·4—155·8° and 155·8—156·1°, under a pressure of 748·9 mm. The purified terebenthene was converted into the monohydrochloride by saturating it with hydrogen chloride at −20°, filtering off the mother liquor at the same temperature, and washing with alcohol; the product may be purified by dissolving in light petroleum, filtering from separated water drops, and allowing to crystallise; it melts at 125°. Terecamphene was first prepared from this hydrochloride by Berthelot, by heating it with sodium stearate; if benzoate or acetate is employed instead of the stearate, inactive camphene is obtained. Alcoholic ammonia is without action on the hydrochloride, and aniline, contrary to the statement of Lauth and Oppenheim (*Bull. Soc. Chim.* [2], **8**, 6), has very little action. The hydrocarbon may be obtained by heating the hydrochloride with an equivalent quantity of sodium acetate and a slight excess of soda in alcoholic solution at 180—200° for 6—8 hours. The corresponding potassium salts have the same effect, but the action is much slower and less complete. When the product is distilled in a current of steam, camphene passes over, and solidifies on cooling. After treatment with soda, distilling over sodium, and repeated crystallisation, it melts at 51—52°, and boils at 158·5—159·5°.

Borneocamphene was prepared from bornyl chloride by Wallach's method, which does not, according to the author, proceed so readily as stated by the former. The product always contains chlorine, and must be purified by treatment with soda and distillation over sodium. It then melts at 53·5—54°, instead of 48—49°, as given by Wallach.

In order to redetermine the physical properties of cymene for comparison with those of the terpenes, this substance was also prepared in quantity from camphor and from cumin oil. From the first source a fraction was obtained boiling at 175—176°, and from the second two fractions boiling at 174·5—175·2° and 175·2—175·9°, under a pressure of 752 mm. H. G. C.

Terpenes and their Derivatives. By J. W. Brühl (*Ber.*, **25**, 151—174).—This paper contains an account of the results of the

spectroscopic examination of the hydrocarbons described in the previous abstract. The results obtained with menthene agree with the supposition that it contains one ethylene linkage, as shown in the constitutional formula given above. In the case of terebenthene (lævopinene), the figures are in agreement with the presence of one para-linkage and one ethylene linkage, thus confirming Wallach's formula. For terecamphene and borneocamphene, the author finds numbers which also agree with the existence of one para-linkage and one ethylene linkage; his previous prediction that camphene would be found to have no ethylene linkage was arrived at from Gladstone's measurements, which differ from those now made. The formula usually accepted for camphene, namely, $CPr^{\beta}\begin{matrix}CH:CH\\ CH_2\cdot CH_2\end{matrix}CMe$, is thus confirmed; but whether terecamphene and borneocamphene are isomeric or identical is at present doubtful. The determination of the heat of combustion of the two substances by Stohmann gave 1466·7 cal. for terecamphene, and 1470·3 cal. for borneocamphene, their manner of burning being also different. It appears, therefore, probable that they are isomeric, but the isomerism is most likely due to differences of position, and not of structure.

The examination of cymene gave results which agree well with those obtained in the case of other benzene derivatives. With methylindene, the figures agree approximately with the formula

$$\begin{matrix}CH{:}C & H\cdot C\cdot CMe\\ CH{:}CH & \cdot C\cdot CH_2\end{matrix}\gtrless CH.$$

H. G. C.

German and Turkish Rose Oils. By C. U. Eckart (*Ber.*, **25**, 311).—In his paper on this subject (this vol., p. 203), the author erroneously gave the old formula for dipentene, whereas, according to Wallach's recent investigations, the latter is a compound of the two optically active limonenes of opposite sign, analogous to racemic acid; accordingly both limonenes must be simultaneously produced from the elæoptene, rhodinol (*loc. cit.*). A. R. L.

Terpenes from the Resin of Pinus abies. By B. Kuriloff (*J. pr. Chem.* [2], **45**, 123—133).—A large quantity of the resin was subjected to steam distillation, and the oil obtained carefully fractionated and freed from products containing oxygen by distillation over sodium. It was separated into two portions boiling at temperatures corresponding with terpene and isoterpene.

The terpene, after careful purification, was quite inactive, and showed no rotatory power when examined in a tube 200 mm. long. It boils at 157° (corr.) under 760 mm. The density is 0·8750 at 0°/4°, and 0·8588 at 20°/4°; coefficient of dilation = 0·00093; molecular refractive power $P\frac{A-1}{d} = 71{\cdot}48$. When treated with hydrogen chloride, it yields a monohydrochloride melting at 126·5°.

The fraction containing the isoterpene, after careful purification, yielded an isoterpene boiling at 176·7° under 772 mm. pressure, and having a specific rotatory power $[\alpha]_D = -47{\cdot}5$. The density is 0·8627 at

0°/4°, and 0·8529 at 20°/4°; coefficient of dilation = 0·00087; molecular refractive power $P\frac{A-1}{d} = 73{\cdot}28$. When treated with hydrogen chloride, it yields a dihydrochloride melting at 48·5°. The quantity of lævorotatory isoterpene obtained only amounted to 2 per cent. of the oil. It corresponds with the dextrorotatory isoterpene obtained by Flawitzky in all particulars, except in the specific rotatation, which is −47·5, whereas dextroisoterpene gives +57·6.

From the above results it is concluded that the oil from *Pinus abies* contains inactive terpene and lævorotatory isoterpene, together with substances containing oxygen which were not examined.

E. C. R.

Camphorone. By W. Koenigs and A. Eppens (*Ber.*, **25**, 260—269).—Gerhardt and Liès Bodart (*Annalen*, **72**, 293) obtained, by distilling calcium camphorate, an oily compound, $C_9H_{14}O$, having a peppermint-like odour, and boiling at 208°, which they named camphorone. Fittig (*Annalen*, **110**, 32; **112**, 311) regarded it as identical with the acetophorone obtained by treating acetone with calcium oxide, as both compounds gave cumene on heating with phosphorus pentoxide. Kachler (this Journal, 1872, 1011), by boiling camphorone with nitric acid, obtained, besides oxalic acid, a crystalline, bibasic acid, $C_6H_{10}O_4$, which he at first believed to be adipic acid, but subsequently stated (*Annalen*, **166**, 320) that it was not.

Camphorone is obtained by distilling dry calcium camphorate, driving over the product in a current of steam, and repeatedly rectifying it, when the chief portion passes over at 195—200° (715 mm.); its composition, $C_9H_{14}O$, was established. The oxime was obtained in a crystalline, but not entirely pure condition. The *bromodibromide*, $C_9H_{11}Br_3O$, is formed when camphorone (2 grams) is dissolved in carbon bisulphide (10 grams) and treated at 0° with a solution of bromine (5 grams) in carbon bisulphide (5 parts); the liquid is washed successively with solutions of sodium hydrogen sulphite and sodium carbonate, and finally with water, the solvent evaporated, and the product allowed to remain in a desiccator under diminished pressure for a while. The yellowish oil, which has a penetrating odour, is then dissolved in alcohol, and water added until the liquid becomes turbid, when colourless needles separate after a time; these are collected and purified by repeated dissolution in alcohol and precipitation with water. The pure compound is odourless, and scarcely soluble in cold water, although readily so in ordinary organic solvents; it commences to sinter at 49°, and melts at 52°, decomposing with the evolution of hydrogen bromide when strongly heated. It will be seen therefore that camphorone behaves towards bromine differently from the crystalline acetophorone (compare Claisen, this Journal, 1876, i, 896). When camphorone (10 grams) is suspended in water, and treated at 0° with potassium permanganate (29 grams) in 4 per cent. aqueous solution, after decolorising the liquid with sodium hydrogen sulphite, driving over any unattacked substance with a current of steam, boiling the filtrate with

animal charcoal, acidifying with dilute sulphuric acid, and distilling, formic and acetic acids pass over, whilst ether extracts a bibasic acid, $C_6H_{10}O_4$, from the residue; this when repeatedly crystallised from benzene melts at 77·5°, and is identical with α-methylglutaric acid (Wislicenus and Limpach, Abstr., 1878, 783; Kiliani, *ibid.*, 1883, 962). It is probable that the acid obtained by Kachler (*loc. cit.*) was also α-methylglutaric acid, but it is not sufficiently characterised by him to decide this question.

The authors adopt the following formulæ for camphoric acid and camphorone respectively (compare Brühl, this vol., p. 202), $\begin{matrix}CH_2\cdot CPr^{\beta}\cdot COOH\\ |\quad\quad |\\ CH_2\cdot CMe\cdot COOH\end{matrix}$ and $\begin{matrix}CH_2\cdot CPr^{\beta}\\ |\quad\quad |\\ CH_2\cdot CMe\end{matrix}>CO$, and they interpret the above described oxidation of the latter as follows:—$\begin{matrix}CH_2\cdot CPr^{\beta}\\ |\quad\quad |\\ CH_2\cdot CMe\end{matrix}>CO + H_2O + 3O_2 = CH_3\cdot COOH + H\cdot COOH + COOH\cdot CH_2\cdot CH_2\cdot CHMe\cdot COOH$.

In conclusion, the authors draw attention to the remarkable resemblance of camphorone to ditetramethylene ketone (Colman and Perkin, Trans., 1887, 236). Both compounds have the same composition, boiling point, and characteristic odour; it is, however, scarcely conceivable, in light of the above formula for camphoric acid, that the two compounds can be identical, and it is difficult to explain the formation of α-methylglutaric acid from ditetramethylene ketone; furthermore, Colman and Perkin obtained a compound of their ketone with sodium hydrogen sulphite, whereas the authors' observations confirm those of Limpricht, that camphorone does not combine with that salt. A. R. L.

Note.—Armstrong and Kipping (Proc., 1891, 188; 1892, 54) have recently separated the ketone 1 : 2 : 4-dimethylacetylbenzene from the product of the action of concentrated sulphuric acid, or of zinc chloride, on camphor. A. R. L.

Puleone, an Isomeride of Camphor. By P. Barbier (*Compt. rend.*, **114**, 126—128).—*Puleone*, $C_{10}H_{16}O$, is the chief constituent of commercial oil of pennyroyal (*Mentha pulegium*, Labiées), from which it may be isolated by repeated fractionations. It is a colourless, mobile liquid which smells strongly of mint, dissolves in alcohol, ether, and benzene, but not in water, boils at 222—223°, and has a sp. gr. of 0·9482 at 0°, and 0·9293 at 23°. It is dextrogyrate, the rotatory power being $[\alpha]_D = +25·25°$. Its index of refraction at 14·9° is 1·4833 and 1·4997, for the tin lines λ 645 and 452·6 respectively. A liquid of the same composition which Kane obtained from the same source (*Phil. Mag.*, **13**, 442) does not appear to be identical, as it boiled at 182—183°.

Puleone, like camphor, contains a carbonyl group, as it combines with hydroxylamine to form an oxime, *puleonoxime*, $C_{10}H_{16}{:}NOH$, which is a colourless liquid having a powerful odour, and boiling at about 170° under a pressure of 48 mm. The oxime is soluble in dilute sulphuric acid, but by boiling this solution is transformed into a very unstable oil of the composition $C_{10}H_{15}N$.

Puleone is oxidised by chromic acid mixture to acetic and carbonic acids, and an acid, $C_7H_{12}O_4$, which crystallises in slender, silky needles, melts at 89—91°, is very soluble in water, alcohol, and ether, and appears to be identical with the propylsuccinic acid obtained by Wurtz from propylethenyltricarboxylic acid (Abstr., 1882, 948). Bromine acts energetically on puleone, hydrogen bromide being evolved, but an additive product is not formed, even at low temperatures and on dilution, so that ethylene linkages do not occur in the molecule. When puleone is treated with phosphoric chloride, hydrogen chloride is evolved, and a liquid derivative, $C_{10}H_{15}Cl$, is formed, and this in turn, when boiled for a long time, loses the elements of hydrogen chloride, and is transformed into a hydrocarbon, $C_{10}H_{14}$, which boils at 177—179°, and appears to be identical with the cymene yielded by camphor under similar treatment.

The formation of propylsuccinic acid from puleone may be held to establish the presence of the group $-C\cdot CHPr^{a}\cdot CH_2\cdot C-$ in the molecule of the latter, and the author thinks, therefore, that it may have the constitution $\begin{matrix} CHPr^{a}\cdot CH\cdot CO \\ | \quad\quad | \\ CH_2 — CH\cdot CHMe \end{matrix}$. Jn. W.

Fraxin and Fraxetin. By G. Koerner and P. Biginelli (*Gazzetta*, **21**, ii, 452—454).—The authors confirm the previous observations on the properties of fraxetin. It melts at 227°, and is found by Zeisel's method to contain one methoxy-group.

Dimethylfraxetin is formed on boiling a solution of fraxetin (2 grams), caustic potash (1·1 gram), and methyl iodide (3 grams) in methyl alcohol for six hours. The alcohol is distilled off, and the solution extracted with ether. On evaporating the ethereal solution, a crystalline product is obtained which separates from dilute alcohol in small, yellowish rhombs, $a : b : c = 0{\cdot}7045 : 1 : 0{\cdot}4096$. It melts at 103—104°. When heated at 100° in a closed tube with potash and methyl iodide, methyl tetramethoxycinnamate is obtained. This substance, on hydrolysis in a closed tube at 100°, yields an acid which is extremely soluble in alcohol, ether, and benzene, sparingly so in cold water. It decomposes carbonates, and gives a barium salt soluble in water. The acid could not be analysed owing to the small quantity obtained.

Fraxetin most probably has the constitution represented by the formula $OMe\cdot C_6H(OH)_2<\begin{matrix} CH:CH \\ O — CO \end{matrix}$, and its glucoside fraxin is therefore $OMe\cdot C_6H(OH)(O\cdot C_6H_{11}O_5)<\begin{matrix} CH:CH \\ O — CO \end{matrix}$. W. J. P.

Pyridine and Piperidine Bases of the β-Series. By C. Stoehr (*J. pr. Chem.* [2], **45**, 20—47; compare Abstr., 1891, 219, 579).—This paper is a summary of the author's work on the β-pyridine bases, and has nearly all appeared before.

The *platinum compound*, $(C_6H_7N)_2,HCl,PtCl_4$, is obtained when β-methylpyridine platinochloride is repeatedly recrystallised; it forms pale-yellow laminæ, and is sparingly soluble in cold water; it begins to melt at 210—212°, but is not fully melted until 220—224°, when it

decomposes. The *zincochloride*, $(C_6H_7N)_2,ZnCl_2$, crystallises in needles, melts at 158°, and dissolves easily in alcohol and water (compare Hesekiel, Abstr., 1886, 256). The *argentonitrate*, $(C_6H_7N)_3,AgNO_3$, crystallises in lustrous prisms which very easily lose some of the base when heated.

β-Methylpiperidine was obtained by the reduction of β-methylpyridine with sodium and alcohol on the water-bath; it boils at 125—126° (mercury column in vapour; 763 mm.), and its sp. gr. at 0°/4° = 0·8635. The *nitrate* crystallises in colourless, hygroscopic laminæ; the hydriodide melts at 158—159° (not 131°, Ladenburg, *Annalen*, **247**, 67); the hydrochloride crystallises from absolute alcohol in thick, colourless aggregates of needles, melts at 171—172°, and is hygroscopic in air (compare Ladenburg, *loc. cit.*).

The platinum compound of ethylpyridine, $(C_7H_9N)_2,HCl,PtCl_4$, melts with decomposition at 240°, not 204—205° (de Coninck, Abstr., 1883, 740). The normal aurochloride, $C_7H_9N,HAuCl_4$, melts at 130°, and the modified aurochloride, $C_7H_9N,AuCl_3$, at 172—174° with decomposition. The picrate melts at 128—130°. The foregoing constants are identical for β-ethylpyridine from brucine and for synthetical β-ethylpyridine, with the exception that the modified platinochloride of the latter melts at 243°. The *cadmioiodide* of *β-ethylpyridine methiodide*, $C_7H_9N_3MeI,CdI_2$, from the synthetical base melts at 125°; the *platinochloride* of the *methochloride* melts, with decomposition, at 210°; the *mercurochloride* of the *methochloride*, $C_7H_9N,MeCl,2HgCl_2$, melts at 85—86°.

In a table, the author compares the melting points and boiling points of β-ethylpyridine from brucine and its derivatives with those of synthetical β-ethylpyridine and its derivatives, and concludes that the two bases are identical.

β-Ethylpiperidine boils at 154—155° (mercury column in vapour); it fumes in the air, and is only slightly soluble in water; its sp. gr. at 0°/4° is 0·8711; it combines readily with carbon bisulphide. The *hydrochloride* forms hygroscopic needles, and melts at 141—142°; the *hydriodide* crystallises in hygroscopic needles, and melts at 123°; the *picrate* forms prismatic needles and prisms melting at 63°; the *platinochloride* forms prismatic crystals (with $\frac{1}{2}$ mol. H_2O), and melts, with decomposition, at 180°; the *aurochloride* forms prismatic needles, and melts at 112°, with decomposition; the *nitrate*, *mercurochloride*, and *cadmioiodide* were obtained. A. G. B.

ββ-Dimethyldipyridyl. By C. Stoehr and M. Wagner (*Ber.*, **24**, 4231—4233).—*ββ-Dimethyldipyridyl* is obtained from β-methylpyridine by a process similar to that employed for the preparation of the αα-derivative (Abstr., 1890, 80; this vol., p. 75); the reaction proceeds in the cold and is complete in about eight days. The product is a dark-coloured liquid mass containing unattacked sodium, and may, without danger of explosion, be added to water; the oily layer is separated, dissolved in ether, the ethereal solution dried over solid potash, and distilled, when about half the β-methylpyridine employed passes over at 170°, the thermometer quickly rising to 250°, and between this temperature and 300° a pale-yellow oil passes over

which quickly solidifies, and is freed from the liquid portion by treatment with a little alcohol and anhydrous ether. The pure compound crystallises from dilute alcohol in large, lustrous, four-sided, anhydrous tables, melts at 125°, sublimes easily, and is only slightly volatile with steam; it is sparingly soluble in hot water, less so in cold, but readily in alcohol and benzene. The *hydrochloride*, $C_{12}H_{12}N_2$,2HCl, separates in small, lustrous crystals, when dry hydrogen chloride is passed into a solution of the base in absolute alcohol; it sublimes without melting, and is very easily soluble in water, its aqueous solutions giving a sparingly soluble bromide on the addition of bromine. The *platinochloride* is very sparingly soluble in water; the *mercurochloride* crystallises from dilute hydrochloric acid in thick, lustrous needles, and melts at 221—222°; whilst the *picrate* separates from its hot aqueous solution in long, lustrous, yellow needles, and melts at 230° with decomposition. The base gives a compound with silver nitrate, sparingly soluble in cold water, readily so in hot, and combines with 2 molecular portions of alkyl halides. The *methiodide*, $C_{12}H_{12}N_2(MeI)_2$, formed by treating the base with methyl iodide at the ordinary temperature, crystallises from boiling alcohol in lustrous, yellowish needles, carbonises at a high temperature without melting, is readily soluble in water, and gives a sparingly soluble *cadmioiodide*. A. R. L.

So-called γ-Bromoquinoline. By H. Decker (*J. pr. Chem.*, [2], **45**, 47—55).—The orientation of the γ′-bromoquinoline of La Coste (Abstr., 1881, 741) and Claus and Collischonn (Abstr., 1887, 159) would be settled if the bromoquinoline could be converted into Baeyer and Bloem's 4′-bromocarbostyril (Abstr., 1883, 196).

For this purpose, 10 grams of the bromoquinoline were dissolved in sulphuric acid, and the solution poured into 5 litres of water; after neutralisation with sodium hydroxide, boric acid, and solution of bleaching powder were added. After one night, *bromopseudochlorocarbostyril*, $C_9H_5BrONCl$, crystallised out. This compound melts about 170° when quickly heated, solidifies again as the heat is continued, and melts finally at 222°; when slowly heated, it melts at 222° only. When it is dissolved in hot concentrated sodium hydroxide solution, sodium bromocarbostyril crystallises on cooling; this is decomposed by water with the formation of bromocarbostyril.

The bromocarbostyril thus obtained crystallises from alcohol in small prisms which melt, at first, at 248°, but at 253° after several recrystallisations. It dissolves in hot alcohol, benzene, hot water, cold concentrated acids, and dilute alkalis. It sublimes unchanged. Baeyer and Bloem's 4′-bromocarbostyril melts at 266°, and is, therefore, not identical with the bromocarbostyril in question, for which the only remaining orientation is 3′-bromo-2′-hydroxyquinoline. The so-called γ-bromoquinoline is thus shown to be 3′-bromoquinoline, and all the compounds which Claus and his co-workers have described as 4′-derivatives are really 3′-derivatives. In support of his position the author compares the behaviour of this bromoquinoline with that of 3-pyridine derivatives, and points out that this bromoquinoline is as stable when heated with water and alkalis or acids as β-bromo-

pyridine; he also points out that Skraup's derivative of kynurin (Abstr., 1890, 174) should be 4′-chloroquinoline. Srpek's orientation of the compound obtained by fusing the bromonicotinic acid derived from this bromoquinoline with potassium hydroxide, as 4′-hydroxypyridine, is pronounced to be rash in the absence of knowledge as to how fusion with potassium hydroxide may alter orientation.

A dibromoquinoline melting at 97°, a tribromoquinoline melting at 174°, and a nitrobromocarbostyril melting, with decomposition, at 308—310°, were prepared in connection with this investigation.

A. G. B.

Benzimidazoles. By E. Bamberger and J. Lorenzen (*Ber.*, **25**, 269—273).—The analogy which might be expected to exist between quinoline and benzimidazole bases is not apparent in so far as the capability of the two for taking up additional hydrogen atoms is concerned, for whereas the former are readily hydrogenised, the latter withstand even the action of concentrated hydriodic acid and phosphorus at a high temperature. It was decided from experiments carried out in the manner given by Niementowski (Abstr., 1886, 544) that the formation of the anhydro-base (methylbenzimidazole) takes place as follows:—$C_6H_4<^{NH_2}_{NH\cdot COMe} = H_2O + C_6H_4<^{NH}_{\ N}>CMe$. This and the two following papers deal with 2 : 2′-dimethylbenzimidazole, a compound obtained by reducing 3 : 4 : 1-nitracetamidomethylbenzene, and with other compounds of the same series, principally to ascertain to what extent the analogy subsists between them and the corresponding quinoline derivatives. Experimental details are reserved for a paper to be published in the *Annalen*. The group NH in benzimidazoles exhibits acidic properties, the hydrogen atom being displaceable by sodium and silver, and when the adjacent group is CH or CPh, the compound even dissolves in aqueous alkalis, and its acidic properties may be still further enhanced by displacing an atom of hydrogen in the benzene nucleus by NO_2. The hydrogen of the NH group may be displaced, through the medium of the silver derivative, by acetyl, but the resulting compound is hydrolysed on boiling it with water; it may also, contrary to Hübner's statement, be displaced by benzoyl, but all attempts have failed to displace it by NO, or the residues –COOEt and –CHMe·COOEt. By the action of bleaching powder on benzimidazoles, chlorimides are produced from which chlorine is evolved at the ordinary temperature on treatment with concentrated hydrochloric acid, and when these are boiled with benzene the chlorine atom is exchanged for an atom of hydrogen in the benzene nucleus; thus the compound $C_6H_3Me<^{NCl}_{\ N}>CMe$ yields $C_6H_2ClMe<^{NH}_{\ N}>CMe$; the latter compound forms a chlorimide, in a similar manner to the original benzimidazole, which undergoes intramolecular change on boiling with benzene, and in this way all the hydrogen of the benzene nucleus may be displaced by chlorine; the ultimate compound, $C_6Cl_3Me<^{NCl}_{\ N}>CMe$, being unattacked by boiling benzene.

A. R. L.

Benzimidazoles. By E. Bamberger and B. Berlé (*Ber.*, **25**, 274—278; 278—281).—2 : 2′-Dimethylbenzimidazole, like 2 : 2′-dimethylquinoline, yields crystalline compounds with phthalic anhydride, benzaldehyde, and chloral, of the formulæ :—

$C_6H_3Me<^{NH}_{N}>C\cdot CH:C_2O_2:C_6H_4$, $C_6H_3Me<^{NH}_{N}>C\cdot CH\cdot CHPh$,

and $C_6H_3Me<^{NH}_{N}>C\cdot CH:CH\cdot CCl_3$ respectively. The two phthalones agree in chemical, physical, and also in tinctorial properties, but the compound of chloral with 2 : 2′-dimethylbenzimidazole is hydrolysed by boiling with water, whereas the corresponding quinoline derivative is not. 2-Methylbenzimidazole yields a coloured condensation product with phthalic anhydride, $C_6H_4:C_2O_2:CH\cdot C_6H_3<^{NH}_{N}>CH$, but it differs in its properties from the phthalones. 3-Methylquinoline yields a crystalline derivative with chloral, which is being investigated, but does not condense with phthalic anhydride. The primary oxidation product of 2 : 2′-dimethylbenzimidazole is the acid $COOH\cdot C_6H_3<^{NH}_{N}>CMe$, which corresponds in its behaviour with 2′ : 2-methylquinolinecarboxylic acid, yields a phthalone, and when passed over heated lime, gives the base $C_6H_4<^{NH}_{N}>CMe$, identical with the anhydro-base obtained from orthonitracetanilide or orthoacetylphenylenediamine; whilst, by more energetic oxidation, the bibasic acid, $COOH\cdot C_6H_3<^{NH}_{N}>C\cdot COOH$, is produced. The acid $C_6H_3Me<^{NH}_{N}>C\cdot COOH$, obtained by carefully oxidising benzylidenimidazole, decomposes by heating into the base $C_6H_3Me<^{NH}_{N}>CH$, which is identical with that obtained from 2 : 3 : 5-diamidotoluene. The authors draw attention to the ease with which the last-mentioned acid, which contains its carboxyl in position 2′, is decomposed, the corresponding quinolinecarboxylic acid exhibiting a similar behaviour. The methylbenzimidazoles containing the methyl group in the benzene nucleus are very readily oxidised; for example, the 2-methyl-derivative is easily converted into the carboxylic acid, which behaves in every respect as the homologue of 2′ : 2-methylbenzimidazolecarboxylic acid (see above). When benzimidazole is oxidised with potassium permanganate, it yields Maquenne's glyoxalinedicarboxylic acid, $CH<^{NH\cdot C\cdot COOH}_{N—C\cdot COOH}$, which, when heated, decomposes into Debus' glyoxaline, the constitution of which may therefore be regarded as $CH<^{NH\cdot CH}_{N—CH}$.

The authors failed to obtain a benzoyl derivative from 2 : 2′-dimethylbenzimidazole. When, however, benzimidazole is treated by the Baumann-Schotten method, it yields a compound, $C_6H_4(NH\cdot CBz)$,

together with formic acid, and this is convertible into Hübner's 2′-phenylbenzimidazole, $C_6H_4<^{NH}_{-N}>CPh$, and benzoic acid. A similar benzoyl derivative is obtained from 2-methylbenzimidazole, which gives Hübner's 2 : 2′-methylphenylbenzimidazole and benzoic acid, and also from nitrobenzimidazole. These reactions are the more remarkable when the stability of the reacting compounds is considered, thus :—bases which withstand the action of alkalis, acids, and reducing agents, and may be heated at a high temperature without alteration, are decomposed as above described by treatment with benzoic chloride and alkali at 0°. A similar case in the quinoline series will be published later, by Bamberger and Williamson. When glyoxaline is treated with benzoic chloride and alkali at 0°, it yields, besides formic acid, dibenzoyldiamidoethylene, $C_2H_2(NHBz)_2$, a compound which crystallises well. These decompositions appear to be dependent on the presence of the group –N·C·N–; pyrroline and pyrazole do not behave in an analogous way. A. R. L.

Etard's Glycoline and Stoehr's Dimethyldiazine. By M. Dennstedt (*Ber.*, **25**, 259—260).—The base obtained by Etard (*Jahresb.*, 1881, 509 and 970) by distilling glycerol with ammonium chloride, to which he gave the name glycoline, is, doubtless, identical with Stoehr's dimethyldiazine (this vol., p. 507) ; it has, most probably, the composition $C_6H_{10}N_2$, and, when treated with nitrous acid, it yields an oil which gives Liebermann's reaction. F. S. K.

Tetrahydropyrazine. By L. Garzino (*Gazzetta*, **21**, ii, 497—504). —A mixture of ethylenediphenyldiamine (10 grams), bromacetophenone (18·7 grams), and anhydrous sodium acetate (7·5 grams) is gradually heated to 100° for half an hour. After cooling, the mass is powdered and extracted with water to remove sodium bromide. The residue is now digested with boiling alcohol (9—10 parts) for 24 hours, washed with alcohol, suspended in water, heated on the water-bath until no further odour of bromacetophenone is observed, and finally evaporated to dryness. On treatment with ether, the greater portion, consisting of a pyrazine derivative, dissolves, whilst a smaller portion (2 grams) remains undissolved, and is purified by digesting for a day with cold alcohol. It is now collected and recrystallised several times from a mixture of alcohol and benzene. In this way *diacetophenonethylenediphenyldiamine*, $C_2H_4(NPh·CH_2·COPh)_2$, is obtained, crystallising in yellow, prismatic needles, and melting at 170—172°. It is very soluble in acetic acid, less so in benzene and chloroform, and only sparingly in alcohol, ether, and carbon bisulphide. It is not decomposed by aqueous potash, but alcoholic potash decomposes it, with formation of a red substance soluble in ether. Its solution in acetic acid turns emerald-green when heated with phenylhydrazine.

The ethereal solution filtered from the crude diacetophenoneethylenediphenyldiamine is evaporated to dryness, dissolved in cold ether, filtered, again evaporated to dryness, and the residue repeatedly crystallised from a mixture of alcohol (9 parts) and

benzene (1 part). Splendid hexagonal scales of *triphenyltetrahydropyrazine*, $PhN<^{CH_2\cdot CH_2}_{CH:PhC}>NPh$, are thus obtained. It melts at 129—131°, and is very soluble in benzene, chloroform, and ether, less so in alcohol. It dissolves to a green solution in acetic acid, and is precipitated unaltered by water from its solutions in hydrochloric and concentrated sulphuric acid. Mercuric chloride, silver nitrate, and auric chloride are reduced by its alcoholic solution; with ferric chloride solution, a green colour, soon turning to intense yellow, is obtained.

If bromacetophenone and ethylenediphenyldiamine are heated together at 100° without sodium acetate, much hydrogen bromide is evolved, but nothing but the unaltered diamine could be separated from the product. Sodium carbonate may be substituted for the sodium acetate without affecting the result. W. J. P.

Synthesis of Pyrazolone Derivatives. By L. Lederer (*J. pr. Chem.* [2], **45**, 83—94).—By the condensation of ethyl acetoacetate and phenylhydrazine, Knorr obtained a phenylmethylpyrazolone which yields antipyrine hydriodide when treated with methyl iodide. He gives to antipyrine the formula $NPh<^{CO—CH}_{NMe\cdot CMe}$. He considers ethyl acetoacetate as a ketone, and hence the phenylmethylpyrazolone has the formula $NPh<^{CO\cdot CH_2}_{N:\ CMe}$, and then he explains the conversion of this compound into antipyrine as due to the formation of an additive compound which undergoes spontaneous molecular change. Nef considers that ethyl acetoacetate behaves as ethyl hydroxycrotonate, and hence arrives at the formula $NPh<^{CO\cdot CH}_{NH\cdot CMe}$ for the pyrazolone derivative, and this formula clearly explains the formation of antipyrine. The author has attempted to settle the question by a synthesis of the pyrazolone from phenylhydrazine and β-halogenbutyric acid. This synthesis requires the formation of symmetrical phenylhydrazinebutyric acid, $NHPh\cdot NH\cdot CHMe\cdot CH_2\cdot COOH$, as primary product, whereas the results show that the asymmetrical compound, $NH_2\cdot NPh\cdot CHMe\cdot CH_2\cdot COOH$, is formed. The latter yields a pyrazolone derivative of the formula $NPh<^{CMe:CH}_{NH\cdot CO}$, and, finally, a compound having a very great resemblance to antipyrine, but not identical with it. The author proposes to call the pyrazolone, $NH<^{CH\cdot CH}_{NH:CO}$, isopyrazolone, and the antipyrine-like compound, isoantipyrine.

Potassium β-bromobutyrate is dissolved in 2½ times the quantity of water, mixed with sodium acetate and the calculated quantity of phenylhydrazine, and allowed to remain in a vacuum at the ordinary temperature for 24 hours. The reaction is completed by warming on the water-bath, the mixture being frequently shaken; after cooling, it

is extracted with ether. The aqueous solution retains most of the phenylhydrazinebutyric acid, which can be extracted with chloroform; whilst phenylmethylhydroisopyrazolone is found in the ethereal solution, and is purified by crystallisation from benzene.

Asymmetrical phenylhydrazinebutyric acid,

$$NH_2{\cdot}NPh{\cdot}CHMe{\cdot}CH_2{\cdot}COOH,$$

crystallises from alcohol in silvery leaflets, melts at 111°, and is easily soluble in hot water, alcohol, and chloroform, but only sparingly in cold water and ether; it quickly reduces silver nitrate and Fehling's solution in the cold, and is stable in the presence of alkalis, less so in the presence of acids.

Phenylmethylhydroisopyrazolone, $NPh<^{CHMe\cdot CH_2}_{NH---CO}$, is obtained by heating the preceding compound (0·5 gram) with concentrated sulphuric acid (2 grams) for $\frac{3}{4}$ hour at 100°. The mixture is diluted with water, neutralised with ammonia, and extracted with chloroform. It crystallises from benzene in two modifications, the stable modification separating in transparent, pale-red, short prisms, whilst the labile forms colourless tablets which become opaque when separated from the solvent. It dissolves easily in chloroform, hot alcohol, and hot benzene, more sparingly in hot water, separates from alcohol in colourless crystals, melts at 127°, dissolves easily in sodium hydroxide, and is reprecipitated by carbonic anhydride. Its solutions turn rose-red on exposure to air. It reduces silver nitrate solution with the production of a blue dye, and gives a carmine-red coloration with sodium nitrite in dilute acetic acid. When methylated, it yields a derivative which melts at 160°, and tastes like antipyrine. The *acetyl* derivative, $NPh<^{CHMe\cdot CH_2}_{NAc---CO}$, is obtained by heating it with acetic anhydride for some hours in a reflux apparatus. It crystallises from ether in colourless, rhomboidal crystals, melts at 79°, is easily hydrolysed by warming with dilute acids and alkalis, and is easily soluble in ether, chloroform, and benzene, sparingly so in water. In neutral solutions, it is stable towards oxidising agents; in alkaline or acid solutions, it is converted into phenylmethylisopyrazolone.

Phenylmethylisopyrazolone, $NPh<^{CMe:CH}_{NH\cdot CO}$, is obtained by adding the calculated quantity of ferric chloride to a warm alcoholic solution of the above hydroisopyrazolone. The mixture is poured into water and extracted with chloroform. On distilling off the chloroform, the isopyrazolone is obtained pure. It crystallises in colourless needles, melts at 167°, and also occurs in another modification which melts at 157° and is easily converted into the first modification. It dissolves in dilute alkalis, is reprecipitated by carbonic anhydride, is easily soluble in benzene, chloroform, and alcohol, sparingly so in water.

Phenyldimethylisopyrazolone (*Isoantipyrine*), $NPh<^{CMe:CH}_{NMe\cdot CO}$, is obtained by heating phenylmethylisopyrazolone with methyl alcohol and a slight excess of methyl iodide in a sealed tube for some hours

at 100°. The alcohol is then distilled off, the residue extracted with water, the solution decolorised with sulphurous acid, precipitated with potassium carbonate, and the isoantipyrine extracted with chloroform. It crystallises in large, yellowish tablets, melts at 113°, is very easily soluble in water and alcohol, easily in chloroform, hot benzene, and hot toluene, but only sparingly in ether, and is a strong base. The *platinochloride* forms dark-yellow crystals, melts at 192°, and is more soluble in water than the corresponding antipyrine derivative. The *picrate* is obtained in bright-yellow needles by mixing aqueous solutions of isoantipyrine and picric acid, and melts about 168°. The *ferrocyanide* is obtained as a white, crystalline precipitate on adding potassium ferrocyanide to a faintly acid solution of isoantipyrine. The *salicylate* is sparingly soluble in water. Isoantipyrine also resembles antipyrine in its behaviour towards ferric chloride, sodium nitrite, nitric acid, and bromine. With ferric chloride, it gives a dark-red coloration. Sodium nitrite colours the faintly acid solution emerald-green; the colour remains unaltered for many hours in dilute solutions; in more concentrated solutions, yellowish-green, oily drops are soon deposited, and by strongly cooling the solution, the *nitroso*-compound can be obtained in moss-green needles which explode at 155°. *Nitroisoantipyrine* is obtained as a crystalline precipitate by dissolving isoantipyrine in cold nitric acid, cautiously warming the solution until it begins to turn red, and then pouring it into water; it melts at 210°. The *bromide* crystallises out on allowing an acetic acid solution of isoantipyrine and bromine to remain for a time. Isoantipyrine does not yield a crystalline compound with benzaldehyde. E. C. R.

Synthesis of 1:3-Phenylpyrrodiazolecarboxylic Acid, 3-Methylpyrrodiazole, 3-Pyrrodiazolecarboxylic Acid, and Pyrrodiazole. By A. Andreocci (*Ber.*, **25**, 225—230).—When 1:3-phenylmethylpyrrodiazole, $\begin{matrix}\mathrm{NPh{\cdot}CH}\\ \|\\ \mathrm{N{=}CMe}\end{matrix}\!\!>\!\mathrm{N}$, is oxidised with potassium permanganate in alkaline solution, it is converted into 1:3-phenylpyrrodiazolecarboxylic acid, which is identical with Bladin's phenyltriazolecarboxylic acid (compare Abstr., 1891, 472). This acid is decomposed on heating, yielding 1-phenylpyrrodiazole, which is, doubtless, identical with Bladin's phenyltriazole; phenylpyrrodiazole melts at 47°, and boils at 266° under a pressure of 760 mm.

Methylpyrrodiazole, $\begin{matrix}\mathrm{NH{\cdot}CH}\\ \|\\ \mathrm{N:CMe}\end{matrix}\!\!>\!\mathrm{N}$, is obtained when 1:3-phenylmethylpyrrodiazole is oxidised with potassium permanganate in acid solution; it is a colourless, crystalline, deliquescent compound, melts at about 93—94°, boils at 265° under a pressure of 760 mm., and is very readily soluble in water and alcohol, but more sparingly in light petroleum; it gives with an ammoniacal solution of silver nitrate an amorphous precipitate, and forms a crystalline platinochloride which is soluble in water.

Pyrrodiazolecarboxylic acid, $\begin{matrix}\mathrm{NH{\cdot}N}\\ \|\\ \mathrm{CH:N}\end{matrix}\!\!>\!\mathrm{C{\cdot}COOH}$, prepared by oxidis-

ing the preceding compound with an alkaline solution of potassium permanganate, is a colourless, crystalline powder, almost insoluble in water, ether, and alcohol, but soluble in alkali carbonates.

Pyrrodiazole, $\begin{matrix}NH\cdot CH\\ \|\quad\ \\ N{=}CH\end{matrix}\!\!>\!N$, is formed when the carboxylic acid is heated alone at 120°, or boiled with water; it melts at 120—121°, boils at 260°, sublimes in needles, and is very readily soluble in water and alcohol, but only moderately easily in ether; it forms compounds with copper, mercury, and silver, and with hydrogen chloride, it yields a crystalline hydrochloride. F. S. K.

Triazole Derivatives. By J. A. Bladin (*Ber.*, 25, 174—183).—In his previous communications, the author has shown that phenylmethyltriazole derivatives are readily obtained by the action of acetic acid on dicyanophenylhydrazine (Abstr., 1885, 980; 1887, 138). Other acid anhydrides may be substituted for acetic anhydride. From the nitriles, $CN\cdot C\!<\!\begin{matrix}NPh\cdot N\\ \|\quad\ \\ N{-}C\,R\end{matrix}$, thus obtained the other derivatives may be prepared in the usual manner.

Phenylethyltriazolecarboxylic acid, $C_2N_3PhEt\cdot COOH$, is obtained from the corresponding nitrile (Abstr., 1885, 980) by boiling it with an excess of potash until no more ammonia is evolved, and carefully adding hydrochloric acid. It crystallises from benzene in small, colourless crystals melting at 144—145°, and from alcohol in large, well-developed crystals melting at 122—123°, the lower melting point being probably due to the presence of water of crystallisation, which is not evolved over sulphuric acid in a vacuum. The *methyl* ether melts at 41°; the *ethyl* ether is a colourless oil; the *alkali* salts are readily soluble in water; the *silver* salt is a white, microcrystalline precipitate; and the *copper* salt, $(C_2N_3PhEt\cdot COO)_2Cu + 3\frac{1}{2}H_2O$, crystallises in lustrous, bluish-green plates, which lose their water of crystallisation at 120°. The *hydrochloride*,

$$C_2N_3PhEt\cdot COOH,HCl,$$

crystallises from boiling hydrochloric acid in small, colourless plates which are decomposed by water.

When the alcoholic solution of the crude nitrile is treated with a few drops of aqueous potash, then with 3 per cent. hydrogen peroxide, warmed, and mixed with hydrochloric acid, it is converted into the corresponding *amide*, $C_2N_3PhEt\cdot CO\cdot NH_2$, which crystallises from alcohol in colourless groups of small prisms, melts at 152—152·5°, and is sparingly soluble in water and ether. The corresponding *thiamide*, $C_2N_3PhEt\cdot CS\cdot NH_2$, is prepared by passing hydrogen sulphide into the alcoholic solution of the crude nitrile, to which a little ammonia has been added; it crystallises in hard, sulphur-yellow prisms, and melts at 149·5—150°.

The nitrile of phenylpropyltriazolecarboxylic acid is readily obtained by heating dicyanophenylhydrazine with butyric anhydride; but as it does not crystallise it was converted at once into the

acid in the manner described under the ethyl derivative. *Phenylpropyltriazolecarboxylic acid*, $C_2N_3PhPr^{\alpha}\cdot COOH$, crystallises from dilute alcohol in colourless, almost cubic crystals, and melts at 160·5—161° with evolution of gas and formation of a colourless oil, which is probably phenylpropyltriazole. It yields a readily soluble *hydrochloride* which is decomposed by water; the *methyl* and *ethyl* salts are colourless oils; the *potassium* and *ammonium* salts are very readily soluble; the *silver* salt forms a voluminous, white precipitate, which readily becomes granular; and the *copper* salt, with $\frac{1}{2}$ mol. H_2O, which is evolved at 170°, forms pale-blue, microscopic needles, the crystals retaining their colour, on further heating, until decomposition commences. The *amide*, $C_2N_3PhPr^{\alpha}\cdot CO\cdot NH_2$, obtained by allowing the methyl or ethyl salts to remain with concentrated ammonia, crystallises from benzene in colourless, spherical groups of prisms, and melts at 122—122·5°; the *thiamide*, $C_2N_3PhPr^{\alpha}\cdot CS\cdot NH_2$, prepared by the action of hydrogen sulphide on an alcoholic solution of the crude nitrile, crystallises from benzene in spherical aggregates of lustrous prisms, and melts at 130—130·5°.

Phenylisopropyltriazolecarboxylic acid, $C_2N_3PhPr^{\beta}\cdot COOH$, is obtained in a manner similar to its lower homologues, and crystallises from benzene in small, colourless prisms containing benzene of crystallisation, which is evolved at 100°, the acid then melting at 135°, with evolution of gas and formation of a colourless oil, apparently phenylisopropyltriazole. The *hydrochloride* forms colourless crystals, and is decomposed by water; the *methyl* salt forms colourless druses of crystals, and melts at 75—76°; the *ethyl* salt is a colourless oil. The *alkali* salts are readily soluble in water; the *silver* salt forms microscopic plates; and the *copper* salt, with $2\frac{1}{2}$ mols. H_2O, forms sky-blue needles which lose their water of crystallisation at 170°, and become emerald-green at 185°. The *amide* crystallises from dilute alcohol in colourless needles, and melts at 127·5—128°; the *thiamide* crystallises from benzene in sulphur-yellow prisms, and melts at 147—148°.

The following substances, analogous to some of those described above, have also been prepared: *the methyl salt of phenylmethyltriazolecarboxylic acid*, which crystallises from dilute alcohol in spherical groups of hard, colourless needles, and melts at 101—105·5°; the *thiamide* of the same acid, which forms sulphur-yellow prisms, and melts at 182°; the *thiamide* of *diphenylthiazolecarboxylic acid*, $C_2N_3Ph_2\cdot CS\cdot NH_2$, which crystallises from benzene in sulphur-yellow needles containing benzene of crystallisation, and loses the latter at 110°, the substance then melting at 170·5—171·5°; and the *thiamide* of *phenylteterazolcarboxylic acid*, $CN_4Ph\cdot CS\cdot NH_2$, which crystallises from alcohol in arge, sulphur-yellow plates, and melts at 168—169°. H. G. C.

Ethyl and Methyl Morphine Carbonates. By R. Otto and A. Holst (*Arch. Pharm.*, **229**, 618—628).—With the potassium derivative of morphine, ethyl and methyl chlorocarbonates react very readily and perfectly. 10 grams of morphine is dissolved in sufficient potassium hydroxide solution (10 per cent.) to allow of a

slight excess of potash being present. Solution of ethyl or methyl chlorocarbonate (10 per cent.) in benzene is added in such quantity that a slight excess of the chlorocarbonate is also present. The two solutions are then agitated together, and the reaction takes place almost instantly, with formation of ethyl or methyl morphine carbonate. The carbonates remain dissolved in the benzene, and, after distilling off the solvent, they are left as yellowish, amorphous, brittle masses, similar to varnish, and become strongly electrical when rubbed. The *methyl* salt, $C_{17}H_{18}NO_2{\cdot}O{\cdot}COOMe$, melts at 116—120°; the *ethyl* compound, $C_{17}H_{18}NO_2{\cdot}O{\cdot}COOEt$, at 113°. In this form they seem to contain benzene. They are readily soluble in benzene, alcohol, ether, chloroform, ethyl acetate, and carbon bisulphide; water dissolves but small quantities, the solutions being strongly alkaline. They react with most of the alkaloïd reagents, but not with tannin. With acids, they react as monacid bases, and form well-defined salts. Those of the *methyl* compound which are described are the *normal sulphate*, a white, crystalline powder, soluble in water and alcohol, and melting at 225°; the *hydrochloride*, very soluble in water; the *platinochloride*, a yellow, crystalline precipitate. The salts of the *ethyl* compound are the *normal sulphate*, the *hydrochloride*, and *platinochloride*, which are similar to the corresponding salts of the methyl compound, and the neutral *oxalate*, a white, crystalline substance, which crystallises with 2 mols. H_2O.

Ethyl and methyl morphine carbonates are decomposed by the alkalis and by ammonia, morphine being set free. The same change occurs by simply boiling the solutions in water, and slowly, by contact with the atmosphere at the ordinary temperature.

The behaviour of these carbonates at a high temperature was examined. It appeared possible that carbonic anhydride might be liberated, with formation of codeïne. Both the compounds yielded carbonic anhydride at 110—120°, in almost exactly the theoretical amount required for the loss of 1 mol. CO_2 from 1 mol. of the base; but no codeïne could be detected in the residue. The residue reacted with the usual alkaloïd reagents. The physiological action of the two double carbonates was somewhat similar to that of codeïne, and dissimilar from that of morphine. J. W. L.

Action of Hydriodic Acid on Cinchonine. By E. Lippmann and F. Fleissner (*Monatsh.*, **12**, 661—666; compare Abstr., 1891, 1517, and Pum, this vol., p. 514).—The authors have repeated some of their experiments on the formation of hydriodocinchonine, $C_{19}H_{23}N_2OI$, with the result that they confirm the statements made in their former communication (this vol., p. 83). Hydriodocinchonine may also be obtained by decomposing in the cold with aqueous ammonia the dihydriodocinchonine, which the authors have prepared by a method similar to that described by Pum (*loc. cit.*). The authors have obtained a compound melting at 187—190°, and apparently indentical with Pum's dihydriodocinchonine, by dissolving in hot alcohol molecular proportions of hydriodocinchonine and dihydriodocinchonine hydriodide (compare Pum, *loc. cit.*). On cooling, a mass of

white needles separated, which, on analysis, gave numbers closely corresponding with those required by the formula $C_{38}H_{48}N_4O_2I_4$.

G. T. M.

Action of Hydriodic Acid on Quinine and on Quinidine. By A. Schubert and Z. H. Skraup (*Monatsh.*, **12**, 669—690; compare Abstr., 1891, 1517; Skraup, this vol., p. 83; and Lippmann and Fleissner, this vol., p. 81).—When anhydrous quinidine is warmed with colourless hydriodic acid of sp. gr. 1·7, and the resulting dark-yellow solution is allowed to remain in the cold for some days, a crystalline mass of reddish-yellow plates is formed which, on treatment with potash, is resolved into the two substances *dihydriodoquinidine hydriodide*, $C_{20}H_{26}N_2O_2I_2,HI$, and *dihydriodoapoquinidine hydriodide*, $C_{19}H_{24}N_2O_2I_2,HI$. If the alkaloïd is heated for three hours at 100° with a more concentrated acid (sp. gr. 1·96), the sole product is dihydriodoapoquinidine hydriodide, whereas if the action takes place at the ordinary temperature, and in absence of light, dihydriodoquinidine hydriodide alone is formed.

Dihydriodoquinidine hydriodide crystallises from alcohol in large, yellow plates, melts at 230°, is insoluble in potash, and, on the addition of alcoholic ammonia at the ordinary temperature, is converted into *dihydriodoquinidine*, $C_{20}H_{26}N_2O_2I_2$. This compound is only slightly soluble in alcohol, and is almost insoluble in water. It melts at 218—220°, decomposes at 228°, and forms an *oxalate*,

$$C_{20}H_{26}N_2O_2I_2,C_2H_2O_4,$$

which crystallises in yellow, microscopic needles, and a hydrochloride, $C_{20}H_{26}N_2O_2I_2,HCl$, which crystallises in small grains.

Dihydriodoapoquinidine hydriodide melts at 252°, is soluble in potash, and, on addition of alcoholic ammonia, furnishes the base $C_{19}H_{24}N_2O_2I_2$, which forms a crystalline *hydrochloride*,

$$C_{19}H_{24}N_2O_2I_2,HCl,$$

and *nitrate*, $C_{19}H_{24}N_2O_2I_2,HNO_3$.

A *base* of the composition $C_{20}H_{24}N_2O_2$, and therefore isomeric with quinidine, is obtained on warming an alcoholic solution of dihydriodoquinidine hydriodide with silver nitrate. It melts at 78—79°, and is dissolved by acids, yielding solutions which have a blue fluorescence and are turned green on the addition of chlorine and ammonia. Dihydriodoapoquinidine, when similarly warmed with silver nitrate, gives the base $C_{19}H_{22}N_2O_2$, which melts at 157°, and forms, with acids, solutions having a slight green fluorescence, and yielding a green coloration with chlorine and ammonia. This base appears also to be formed on long-continued heating of dihydriodoapoquinidine (1 mol.) with aniline (3 mols.) at 100°.

When anhydrous quinine is heated at 100° with hydriodic acid of sp. gr. 1·7, a substance which melts at 228—230°, and gives numbers corresponding with the formula $C_{20}H_{24}N_2O_2,3HI$ (compare Lippmann and Fleissner, *loc. cit.*), is obtained. It appears to be a mixture, since, on treatment with cold alcoholic ammonia, it yields two distinct bases having the composition $C_{20}H_{25}N_2O_2I$ and $C_{20}H_{26}N_2O_2I_2$, respectively. The former, *hydriodoquinine*, the chief product, is

soluble in alcohol, but almost insoluble in ether, and melts at 155—160°, with decomposition; its solution in dilute acids shows a blue fluorescence, and gives a brownish-yellow precipitate with chlorine and ammonia.

If quinine is treated with a stronger acid (sp. gr. 1·96), methyl iodide is evolved, and a substance of the composition $C_{19}H_{22}N_2O_2,3HI$ obtained. It melts at 236—238°, is insoluble in potash, and is most probably a mixture of $C_{19}H_{23}N_2O_2I,2HI$ and $C_{19}H_{24}N_2O_2I_2,HI$, since it gives with alcoholic ammonia in the cold the two bases $C_{19}H_{24}N_2O_2I_2$ and $C_{19}H_{23}N_2O_2I$ respectively. The former is the chief product; the latter gives a bright yellow *oxalate*, $C_{19}H_{23}N_2O_2I,C_2H_2O_4$, which melts at about 187°. G. T. M.

Alkaloïds of Berberis aquifolium and B. vulgaris. By C. Rüdel (*Arch. Pharm.*, **229**, 631—666).—The publications of Wacker, of Hesse, and of Stubbe, on the alkaloïds of the roots of *Berberis vulgaris*, and those of Parsons (Abstr., 1882, 1140), of Jungk, and of Stubbe on the alkaloïds of the roots of *Berberis aquifolium* show that each contains three alkaloïds, and that they are in all probability the same. The chemical formula and the exact description of the salts were not, however, very perfectly defined, and the author has endeavoured to complete this part of the work.

The ground-up roots were in each case extracted with very dilute acetic acid, and the extract was then concentrated to a syrup. Oxyacanthine was precipitated by sodium sulphate, berberine as acetone-berberine (Gaze's method) and berbamine by the addition of sodium nitrate.

Oxyacanthine, $C_{19}H_{21}NO_3$.—The elementary analyses of the specimens of this alkaloïd, as obtained from the two different sources, agreed closely with the above formula. The melting point lay between 174° and 185°; the base appears to exist in an amorphous and in a crystalline modification. It reacts with the usual alkaloïd reagents. The salts prepared were the normal *sulphate*,

$$(C_{19}H_{21}NO_3)_2,H_2SO_4 + 4H_2O,$$

white and crystalline; the hydrochloride, $C_{19}H_{21}NO_3,HCl + 2H_2O$, prepared from the platinochloride by precipitating the platinum with hydrogen sulphide, white and crystalline; the platinochloride, $(C_{19}H_{21}NO_3)_2,H_2PtCl_6 + 5H_2O$, a yellow, amorphous salt which could not be obtained crystalline; and the aurochloride, $C_{19}H_{21}NO_3,HAuCl_4 + 4H_2O$, a golden-yellow, amorphous substance, which likewise could not be obtained crystalline. These salts of oxyacanthine from different sources were alike in all respects.

Berbamine, $C_{18}H_{19}NO_3$, separated from the solution of the alkaloïds by the addition of sodium nitrate, was purified by precipitating the solution of the sulphate with ammonia and recrystallising from anhydrous ether. Thus obtained, it forms a fine, white, crystalline mass. The specimens from both sources proved to be identical. The following salts were prepared; the normal sulphate,

$$(C_{18}H_{19}NO_3)_2,H_2SO_4 + 4H_2O,$$

crystalline; the platinochloride, $(C_{18}H_{19}NO_3)_2,H_2PtCl_6 + 5H_2O$, a light-

yellow, amorphous powder; and the aurochloride, $C_{18}H_{19}NO_3,HAuCl_4 + 5H_2O$, a golden-yellow, amorphous powder.

Berberine, $C_{20}H_{17}NO_4$, was most readily separated by Gaze's acetone method. Acetoneberberine, $C_{20}H_{17}NO_4,C_3H_6O$, was obtained as a lemon-yellow, crystalline powder; acid berberine sulphate, $C_{20}H_{17}NO_4,H_2SO_4$, prepared by treating acetoneberberine with dilute sulphuric acid, is a pale-yellow, crystalline salt; the nitrate, $C_{20}H_{17}NO_4,HNO_3$, prepared by treating the acetone compound with the exact quantity of nitric acid, is a crystalline, yellowish-red salt; the platinochloride,

$$(C_{20}H_{17}NO_4)_2,H_2PtCl_6 + H_2O,$$

prepared by precipitating the hot solution of the hydrochloride with platinum chloride, is obtained as a yellow, crystalline precipitate; the hydrochloride, $C_{20}H_{17}NO_4,HCl + 4H_2O$, obtained by decomposing the acetone compound with hydrochloric acid, is a light orange-yellow-coloured salt.

Since Gaze found a "methylberberine" accompanying the berberine which he obtained from hydrastis berberine, the author converted a considerable quantity of his berberine specimen into hydroberberine, by reduction with zinc and sulphuric acid, and searched very carefully among the crystals of hydroberberine which were obtained for any second substance. No such other alkaloïd could, however, be found. J. W. L.

Constituents of Angostura Bark. By H. Beckurts and P. Nehring (*Arch. Pharm.*, **229**, 591—617).—The bark of the Columbian rutacea, *Cusparia trifoliata*, Engler (*Galipea officinalis*, Hancock), has been examined by the authors.

30 kilos. of the coarsely-powdered bark was extracted with 75 kilos. of ether; most of the ether was then distilled off, and the brown residue extracted with dilute sulphuric acid. Wax and essential oils were thus separated from the alkaloïds, and, in addition, a greenish-yellow, crystalline substance was precipitated; it is the salt of a base or bases, but it could not be obtained pure.

From the acid solution, four alkaloïds, *cusparine*, *cusparidine*, *galipine*, and *galipidine* were separated. The separation of these was, however, exceptionally difficult, since their solubilities are very similar, and they were obtained pure only by means of (1) repeated fractional crystallisation from their solutions in light petroleum; (2) fractional crystallisation of the respective sulphates from hot aqueous solution.

The residual bark, after extraction with ether, was extracted with 60 kilos. of alcohol, and the alkaloïds, wax, and oils separated from each other as from the ether extract. The same four alkaloïds were again obtained. The total quantity of impure bases which was thus separated amounted to 595 grams, or 2·0 per cent.

Galipine, $C_{20}H_{21}NO_3$, crystallises from light petroleum in slender, lustrous, soft needles which are pure white. It melts at 115·5°. It dissolves very readily in alcohol, chloroform, acetone, benzene, and ether, but is only sparingly soluble in light petroleum. Its salts are yellow, and crystallise like the base. The *hydrochloride*,

$$C_{20}H_{21}NO_3,HCl,4H_2O,$$

forms lustrous, yellow plates, very soluble in warm water. The *hydrobromide*, $C_{20}H_{21}NO_3,HBr$, crystallises in deep-yellow needles, and is very soluble in water and alcohol. The *hydrogen sulphate*, $C_{20}H_{21}NO_3,H_2SO_4$, forms lustrous, yellow needles. The *platinochloride*, $(C_{10}H_{21}NO_3)_2,H_2PtCl_6$, melts at 174—175°, crystallises in very small, yellow needles, and is almost insoluble in alcohol and in water. The *aurochloride*, $C_{20}H_{21}NO_3,HAuCl_4$, melts at 175—176°, and crystallises in very small, brownish-red needles. The *methiodide*, $C_{20}H_{21}NO_3,MeI$, forms small, lemon-yellow needles which melt at 146°; it is soluble in alcohol and in hot water, insoluble in ether.

Galipidine, $C_{19}H_{19}NO_3$, crystallises from light petroleum in very light, silky, lustrous plates which are pure white. It is readily soluble in alcohol, ether, benzene, ethyl acetate, and chloroform, less soluble in light petroleum; it melts at 111°. The salts are pale yellow, are readily soluble in hot water, and the solutions have a bitter taste. The *hydrochloride*, $C_{19}H_{19}NO_3,HCl + 3H_2O$, forms pale-yellow needles, soluble in warm water, but only sparingly soluble in cold water; the *hydrobromide*, $C_{19}H_{19}NO_3,HBr$, crystallises in minute, pale-yellow needles, readily soluble in water and alcohol; the *aurochloride*, $C_{19}H_{19}NO_3,HAuCl_4$, is precipitated as a mass of minute, chocolate-brown needles; it melts at 167°, and is almost insoluble in water and alcohol; the *platinochloride*, $(C_{19}H_{19}NO_3)_2,H_2PtCl_6$, separates as a voluminous, yellow, crystalline precipitate, very sparingly soluble in water; it melts at 182°. The *methiodide*, $C_{19}H_{19}NO_3,MeI$, forms a fine, yellow, crystalline powder, readily soluble in hot water and alcohol; it melts at 142°, and has an intensely bitter taste.

Cusparine, $C_{20}H_{19}NO_3$, is comparatively easily separated from the other bases, owing to the sparing solubility of its salts. It melts at 89°, and is readily soluble in alcohol, ether, choloroform, acetone, and benzene, more sparingly in light petroleum. Its salts are white and sparingly soluble in water, more readily in alcohol. The *hydrochloride*, $C_{20}H_{19}NO_3,HCl + 3H_2O$, crystallises in long, white needles, very slightly soluble in water, readily in alcohol, and of a bitter taste; the *hydrobromide*, $C_{20}H_{19}NO_3,HBr$, forms long, pale-yellow needles, of bitter taste; it is very sparingly soluble in water; the *sulphate*, $(C_{20}H_{19}NO_3)_2,H_2SO_4 + 7H_2O$, crystallises in white prisms of a bitter taste; it is only sparingly soluble in water, more readily in alcohol; the *aurochloride*, $C_{20}H_{19}NO_3,HAuCl_4$, forms a light-brown, voluminous mass of minute crystals, melts at 165°, and it is almost insoluble in water; the *platinochloride*, $(C_{20}H_{19}NO_3)_2,H_2PtCl_6$, forms minute, yellow needles, which may be recrystallised from hot water. It melts at 179°. The *methiodide*, $C_{20}H_{19}NO_3MeI$, forms lustrous, yellow needles, of intensely bitter taste, melting at 186°.

Cusparidine, $C_{19}H_{17}NO_3$, crystallises from light petroleum in minute, slender, white needles. It melts at 78°, and dissolves readily in chloroform, alcohol, ether, and ethyl acetate, less readily in light petroleum. The salts are white and of bitter taste; they are less soluble than those of galipine and galipidine, but more readily than those of cusparine. The *hydrochloride*, $C_{19}H_{17}NO_3,HCl + 3H_2O$, is precipitated as a white, voluminous mass of crystals, which melt very readily; it is sparingly soluble in water, more readily in alcohol,

and has a bitter taste. The *hydrobromide*, $C_{19}H_{17}NO_3,HBr$, crystallises from water in well-formed prisms, which are anhydrous; it is sparingly soluble in hot water, almost insoluble in cold water, more readily soluble in alcohol. The *sulphate*, $(C_{19}H_{17}NO_3)_2,H_2SO_4 + 3H_2O$, separates as a crystalline precipitate when cusparidine is exactly neutralised with sulphuric acid; it is moderately soluble in water, still more readily in alcohol, and has a very bitter taste. The *aurochloride*, $C_{19}H_{17}NO_3,HAuCl_4$, separates as a voluminous, brown mass of minute crystals; it is anhydrous, and melts at 167°. The platinochloride, $(C_{19}H_{17}NO_3)_2,H_2PtCl_6$, forms a pale-yellow, crystalline precipitate, which is insoluble in water and alcohol; it melts at 182°. The *methiodide*, $C_{19}H_{17}NO_3MeI$, is prepared by heating cusparidine with excess of methyl iodide for three hours at 100° in a sealed tube; after recrystallising from water, it forms a pale-yellow, crystalline powder, soluble in water and alcohol, insoluble in ether. It has a very bitter taste; its colour changes to brown on exposure to the air or light, and it melts at 149°.

The four alkaloïds are tertiary bases; their reactions with the various alkaloïdal reagents are described.

The *essential oil* of angostura bark, which was extracted by means of ether, was freed from alkaloïds by dilute sulphuric acid, and then remained as a dark-coloured liquid. From 100 kilos. of the bark, 1·5 kilos. of the oil was obtained. It has an aromatic odour: the sp. gr. at 15° is 0·956, and it dissolves in ether, alcohol, chloroform, light petroleum, and glacial acetic acid; it reddens litmus. It is free from sulphur and nitrogen, and does not react either as a phenol, a ketone, or an aldehyde. Distilled under a pressure of 35 mm., it commences to boil at 153°; the greater part distilled between 200° and 220°; the last portions became solid when cooled with a mixture of sodium sulphate and hydrochloric acid.

The *bitter principle*, *angosturin*, is insoluble in ether, but soluble in alcohol, and is found therefore in the alcoholic extract of the bark; it is obtained free from alkaloïds after the alcoholic extract has been rendered alkaline with sodium carbonate and extracted with ether. The bitter principle is difficult to obtain pure. The residue, after separating the alkaloïds, was dissolved in water, and an excess of tannin added; the precipitate was washed with water, and dissolved in alcohol; lead acetate was added, and the precipitate first washed with alcohol and then with boiling water. The angosturin was further purified by dissolving it in water, precipitating with charcoal, extracting with alcohol, and finally evaporating the latter. It remained as a transparent, pale-yellow mass, which is soluble in water, alcohol, and glacial acetic acid. The addition of ether to the solution in acetic acid precipitated the angosturin quite white; it melts at 58°.

The angostura bark contains a *glucoside*, which may be separated from the bark, after exhausting it first with ether, and then with alcohol, by extraction with water. The solution fluoresces and reduces Fehling's and other metallic solutions. The glucoside was not however obtained pure. J. W. L.

Ash-free Albumin. By E. Harnack (*Ber.*, **25**, 204—209; compare Abstr., 1891, 476; also Werigo, Abstr., 1891, 1268, and Stohmann and Langbein, this vol., p. 4).—The author points out that the ash-free albumin prepared by his method has none of the characteristic properties of an acid albumin in spite of the fact that it contains hydrochloric acid; he considers that his ash-free albumin may be ordinary albumin freed from inorganic bases, &c., and combined with hydrochloric acid without any alteration of the molecule, just as in the case of the hydrochlorides of amido-acids.

Preparations of ash-free albumin which have been repeatedly dissolved and reprecipitated and then well washed contain 1·4 per cent. of chlorine, which corresponds with 2 mols. of hydrogen chloride to 3 atoms of sulphur in the albumin molecule. When the ash-free albumin is submitted to dialysis, the hydrochloric acid passes away, and the albumin gradually separates from the solution in the form of a transparent jelly; if the water containing the jelly is heated to boiling, the albumin becomes white, compact, and crystalline in appearance, especially after drying; the same effect is produced when the jelly is treated with alcohol. The crystalline powder obtained in this way is insoluble in water, but dissolves at once on the addition of a trace of hydrochloric acid, the solution having the properties of a solution of the original ash-free albumin. F. S. K.

Rotatory Power of Various Silks. By L. Vignon (*Compt. rend.*, **114**, 129—131).—The specimens were dissolved in the manner previously described (this vol., p. 254), with the exception that in one case sulphuric acid was substituted for hydrochloric acid.

The solutions were lævogyrate in all cases, the values of $[\alpha]_j$ at 15° varying from −9° to −43·6° for the alkaline solutions, the mean being −29·6°, and from −39·4° to −50° for the acid solutions, the mean being −44°. Jn. W.

Physiological Chemistry.

Digestibility of Pentose Carbohydrates. By W. E. Stone (*Amer. Chem. J.*, **14**, 9—14).—Rabbits were fed during the first period with a mixture of bran and meal; during the second, with bran only. A complete analysis was made in each case of the food and of the dung, the pentosans or pentose carbohydrates being estimated in the "nitrogen-free extract" by converting them into furfuraldehyde and titrating this with a standard solution of phenylhydrazine (pentosans = furfuraldehyde × 1·38). The pentosans are much less digestible than the true carbohydrates. In the first period, about 60 per cent. was digested; but in the second period, when the proportion of nitrogenous to carbonaceous matter was considerably increased, the pentosans did not seem able to supply

the lack of carbohydrates, and were themselves digested to a less extent than 40 per cent. The proportion of pentosans in the nitrogen-free extract of the dung is much higher than in that of the food; thus the digestive action has been selective, and only certain constituents of the nitrogen-free extract of the food have been removed, whilst others remain wholly or in part unchanged. C. F. B.

Absorption without Osmosis. By E. W. Reid (*Brit. Med. J.*, i, 1892, 323—326).—In a previous paper (Abstr., 1890, 277), it was shown that in the skin of the living frog, the osmotic transfer of liquid occurred in one direction, namely, from without inwards, that whatever raised its vitality increased the flow, and whatever depressed it diminished the flow. The evidence of the existence of vital absorptive force would be stronger if one could put osmosis entirely on one side and actually observe the passage of liquid across the living skin by virtue of its own unaided activity. This can be effected by an apparatus which is figured and described in the present communication. Briefly, it consists of a cylinder placed horizontally, across the middle of which a diaphragm of live skin is placed; both sides are filled with salt solution, and the transfer of liquid watched in fine manometers, also running horizontally, one on each side of the membrane. The liquid falls in one, that facing the outer surface of the skin, as it rises in the other. This is not osmosis, filtration, or electro-osmosis, but a special non-osmotic vital absorptive power. W. D. H.

Tissue-Fibrinogens. By A. E. Wright (*Proc. Roy. Irish Acad.* [3], **2**, No. 2).—In a previous communication, Wooldridge's "tissue-fibrinogens" were stated to consist chiefly of nucleo-albumin. These substances were said to give the biuret reaction characteristic of proteoses and peptones, and the theory advanced that in the body a peptone-like substance is split off from the proteïd. This is now supported by experiments which show that in animals, after the intravenous injection of tissue-fibrinogens, there is at a certain stage not only the increased coagulability of the blood noted by Wooldridge, but also a diminished coagulability, such as is produced by peptone. Moreover, "peptonuria" also occurs. W. D. H.

Formation of Uric Acid from Nucleïn. By J. Horbaczewski (*Sitz. k.k. Akad. d. Wiss. Wien. Mathem.-naturw. Cl.*, 1891, Abth. 3).—By treating splenic pulp with blood, uric acid is formed. If fresh pulp is allowed to digest with water for 8—10 hours until an odour of putrefaction is just observable, and then lead acetate added, and the mixture filtered, the filtrate when mixed with blood leads to the formation of uric acid. If, however, the filtrate is boiled first, no uric acid, but an equivalent of xanthine and hypoxanthine, is formed.

Recent researches having shown that nitrogenous bases are obtained from nucleïn, the idea arose that the nucleïn of the splenic cells might be the source of the uric acid, and, in fact, nucleïn (prepared as an insoluble residue after the gastric digestion of splenic

pulp) yielded uric acid just as splenic pulp does. Uric acid was also found to be obtainable from any organ rich in nuclei.

The next step in the investigation showed that uric acid was increased in the urine of animals after food, and especially by food which, like meat, causes an increase of leucocytes in the blood. Subcutaneous injection of nucleïn led to a great increase in the uric acid excreted. This occurs both in animals and in men. In certain cases of disease in man in which no increase of leucocytes occurred, there was also no rise in the uric acid eliminated.

The influence of drugs was also investigated. Quinine produces a fall in the number of leucocytes, and a fall also in the excretion of uric acid. Atropine acts in the same way. Pilocarpine produces the opposite effect. Antipyrin and antifebrin produce an increase of leucocytes, but a fall in the uric acid; this is explained by the hypothesis that although the leucocytes are more numerous, they are not destroyed so rapidly. Microscopic examination of the spleen and blood showed the leucocytes in an atrophic condition after quinine and atropine, whilst after pilocarpine they are undergoing karyokinetic changes.

Lastly, the condition of things in various pathological conditions showed that wherever there is leucocytosis or leucocythæmia there also is an increase in the output of uric acid; and the theory that it originates from nucleïn is considered to be borne out very fully.

W. D. H.

Influence of Various Salts on Live Weight and on the Composition of Bones and Teeth. By H. Weiske (*Landw. Versuchs-Stat.*, **40**, 81—108; compare Abstr., 1891, 848 and 1525). —The experiments now described were made in order to ascertain whether calcium carbonate, or salts having an alkaline reaction, or organic salts, have the same effect as hay (or other foods which give alkaline ashes) in hindering the extraction of minerals observed with foods which yield acid ashes. As in the earlier experiments, rabbits were used; they were fed on oats alone, and on oats with the addition of one of the following salts:—calcium carbonate, tricalcium phosphate, sodium phosphate, sodium dihydrogen phosphate, sodium citrate. With regard to increase in weight, it was found that oats alone is unsuitable; oats with hay, with calcium carbonate (and possibly calcium phosphate), and in one case with sodium phosphate, gave satisfactory results, whilst the other salts were more or less injurious. With the addition of hay or calcium carbonate to oats, the rabbits remained healthy and increased in weight, and the bones increased both in weight and strength. Both the calcium carbonate and the minerals of the hay tend to neutralise the acids of oats, and both contribute to increase the lime in the bones. The fact that one of the rabbits which had calcium phosphate lost weight makes it probable that want of lime was not the only cause of the unsatisfactory results obtained by the exclusive use of oats. Sodium dihydrogen phosphate produced loss of weight, and the bones became poorer in minerals, thin-walled, and weaker. Sodium citrate gave rise to a greater loss of total weight, and of the weight of the bones, than was

the case with oats alone; the bones were also poorer in minerals. The composition of the teeth varied only slightly in all the experiments.

Tables are given showing the weights of the rabbits during the experiments, the amount of flesh found after they were killed, the composition of the ash of the flesh, and the weight and composition (organic matter and ash constituents) of the bones. N. H. M.

Blood of Invertebrata. By A. B. Griffiths (*Proc. Roy. Soc. Edin.*, **18**, 288—294).—The gases of the blood of various invertebrates investigated by the use of the mercurial air-pump, gave the following results:—

Animal.	Oxygen.	Carbonic anhydride.	Nitrogen.
Sepia officinalis	12·9—13·6	29·1—32·1	1·2—2·0
Cancer pagurus	14·7—14·9	27·1—28·6	1·0—1·3
Palinurus vulgaris	14·2—14·7	28·9—30·0	1·2—1·8
Homarus vulgaris	14·8—14·9	28·8—31·1	1·7—1·8
Octopus vulgaris	13·2—13·6	30·2—31·2	1·3—1·4
Acherontia atropos	16·2—16·7	32·9—34·2	1·1—1·9

The oxygen and carbonic anhydride, as in vertebrates, thus do not obey Dalton's law, but are in part in chemical combination; the oxygen being held by hæmocyanin, a copper-containing proteïd, which takes the place of hæmoglobin in these animals.

The mineral matter of the blood was examined in a number of invertebrates; in gastropods, its amount was 1·1 to 1·8 per cent.; in *Sepia* the percentage was 2·8; in *Octopus* 3.

The following table gives a few results, selected from the fuller tables in the paper:—

	Cancer pagurus.	*Astacus fluvatilis.*	*Homarus vulgaris.*	*Anodonta cygnea.*	*Octopus vulgaris.*
CuO	0·22	0·2	0·18	0·23	0·21
Fe_2O_3	trace	0	trace	0	0
CaO	3·55	3·58	3·54	3·61	2·40
MgO	1·91	1·88	1·89	1·82	1·55
K_2O	4·97	4·82	4·77	4·90	4·90
Na_2O	43·9	44·96	44·99	44·18	45·31
P_2O_5	4·9	4·81	4·84	4·89	4·88
SO_3	2·9	2·75	2·81	2·80	2·83
Cl	37·65	37·0	36·96	37·55	37·92

In addition, it may be mentioned that in the blood of *Anodon* a trace of lithium was detected by the spectroscope; that in *Mytilus edulis* a trace of manganese was found, in addition to the usual (0·22)

percentage of copper, while in *Pinna squamosa* the percentage of manganese was 0·19, and only a trace of copper was found.

W. D. H.

Carbonic Anhydride in the Urine. By T. C. Van Nüys and R. E. Lyons (*Amer. Chem. J.*, **14**, 14—19).—The normal urates of sodium and potassium ($C_5H_2N_4K_2O_3$, $C_5H_2N_4Na_2O_3$) are strongly alkaline; they are decomposed by carbonic anhydride or acid calcium phosphate, $CaH_4(PO_4)_2$, with formation of the acid urates, which are themselves further decomposed, uric acid being deposited. Carbonates are decomposed by acid sodium or calcium phosphate; hence carbonic anhydride can hardly exist combined in urine, unless the latter is strongly alkaline.

The carbonic anhydride in the urine was estimated after employing (1) a mixed diet, (2) a vegetable diet, (3) after ingesting large doses of normal sodium tartrate, $C_4H_4Na_2O_6$. With (1) the urine was acid in reaction, and contained a relatively small quantity of carbonic anhydride; with (2) it was strongly alkaline, and contained more carbonic anhydride; with (3) it was strongly alkaline, owing partly to alkali carbonates, for it effervesced with acids.

The following conclusions are drawn:—(1) Combined carbonic anhydride is not ordinarily a constituent of normal urine. (2) When carbonic anhydride does appear in the urine combined, it is owing to excessive alkalinity of the blood, when it is induced to combine with the hydroxides of potassium and sodium which would otherwise appear in the urine. (3) The alkalinity of normal urine, unless excessive in degree, is caused by di- or tri-basic potassium or sodium phosphates, and by normal urates of potassium and sodium.

C. F. B.

Hæmatoporphyrin in Urine. By O. Hammarsten (*Skand. Arch. f. Physiol.*, **3**, 319—343).—This is a very thorough investigation of the urine in four cases of hæmatoporphyrinuria, in which the pigments were all separated, and the hæmatoporphyrin crystallised as a hydrochloride.

The cases were all women suffering from melancholia or mania, and were all treated with sulphonal. More observations are, however, necessary before it can be absolutely proved that the drug is the cause of the pigment in the urine.

Urine No. 1.—The pigments found were:—(1) Urobilin. (2) A yellow pigment, probably identical with that in normal urine. (3) Hæmatoporphyrin. (4) A red-brown pigment which gives no fluorescence with zinc chloride and ammonia, and so does not belong to the urobilin group.

Urine No. 2.—The pigments (1), (2), and (3) were the same as in urine No. 1. (4) A red-brown pigment similar to Le Nobel's hexahydrohæmatoporphyrin (*Pflüger's Archiv*, **11**). (5) A chromogen of a pigment of the urobilin group. (6) A chromogen which, on the addition of acid, yields a rose-red pigment which, however, is not identical with indigo-red or uroseïn.

Urines Nos. 3 *and* 4.—In the main the same as urine No. 1.

W. D. H.

The Urine in a Case of Phosphorus Poisoning. By E. H. Starling and F. G. Hopkins (*Guy's Hosp. Rep.*, 1890, 275—278).—In a case of phosphorus poisoning, which proved fatal in a few days, the urine gave the following analytical results:—

Urea	2·5	per cent.	
Ammonia	0·18	,,	
Total nitrogen	1·344	,,	
Nitrogen as urea	1·17	,,	ratio 7·9 : 1.
,, ammonia	0·148	,,	
Leucine and tyrosine	none		
Total sulphur	0·24	,,	
Oxidised sulphur	0·122	,,	0·116 as sulphates. 0·006 as ethereal sulphates.
Ratio of unoxidised to oxidised sulphur			0·97 : 1.
Total amount of urine in 12 hours			528 c.c.

The urine is thus nearly normal; the deviations from the normal being the large amount of nitrogen as ammonia and of sulphur in the unoxidised condition. The former is probably due to diminished alkalescence of the blood, as evidenced by the decrease of carbonic anhydride there (Meyer, *Arch. exp. Path. Pharm.*, **14**, 313).

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Ferments in Pineapple Juice. By R. H. Chittenden, E. P. Joslin, and F. S. Meara (*Trans. Connecticut Acad.*, **8**, 1—28).—Papaïn is the best known instance of a proteolytic ferment in the vegetable kingdom; recent research shows that such ferments are almost universally distributed, and that that in pineapple juice is very remarkable in its powers. The juice itself is acid, and contains a small amount of proteïd matter (less than 0·025 per cent.) which consists of three proteïds, one coagulated at 75°, another at 100°, and a small amount of non-coagulable proteose.

The proteolytic action of the juice tested on flesh, fibrin, white of egg, &c., takes place in an acid, alkaline, or best in a neutral medium, and at a temperature of 40°. The juice has also the power of curdling milk like rennet.

Saturation with ammonium sulphate precipitates all the proteïds in the juice, and with them the ferment or ferments. The proteïd precipitate, freed from excess of salt by dialysis, acts on proteïds like the original juice. Sodium chloride also precipitates a proteïd having characters akin to globulin and to heteroproteose; this is either the ferment or closely associated with it.

W. D. H.

Action of Boric Acid on Germination. By J. Morel (*Compt. rend.*, **114**, 131—133).—The rate of germination of beans and wheat which have been soaked in aqueous solutions of boric acid or borax (0·01—0·1 per cent. of acid) is considerably less than the normal, the amount of retardation increasing with the strength of the solution. The plants which subsequently develop from the seedings are weakly, and etiolated in the same proportion. Jn. W.

Sodium Chloride in Plants. By P. Lesage (*Compt. rend.*, **114**, 143—145).—By watering certain plants, such as *Lepidium sativum* and *Raphanus sativus*, with sea-water or salt solution the author recently succeeded in producing modifications in them identical with those which they undergo naturally when they are allowed to grow near the sea-coast. He now finds that sodium chloride is actually absorbed by the plants thus artificially modified, an excessive amount of sodium, for instance, being found in the stems of the first-named plant, and in the tubers of the other. Jn. W.

Absence of Oxalates in Young Leaves, as in the case of some Phanerogam Parasites. By C. Wehmer (*Land. Versuchs-Stat.*, **40**, 109—159).—Crystals of calcium oxalate occur in nearly all the cells of quite young leaves developed at the beginning of summer; in the case of leaves which develop in the early spring, the same leaf in its first and last stages is free from them. This is readily seen in the case of *Symphoricarpus racemosa*, and has been observed by the author in the case of many woody plants. The present investigation was undertaken with a view to ascertain whether in the absence of microscopically visible calcium oxalate, the salt (or oxalic acid) is really absent, or whether it is present in another form. Young leaves of the following species were examined:—*Symphoricarpus racemosa*, *Cratægus oxyacantha*, *Æsculus hippocastanum*, *Sambucus nigra*, *Prunus Padus*, *Juglans regia*, and *Aspidium filix mas*. The methods employed for the identification of lime and oxalic acid are fully described.

Æsculus hippocastanum.—The leaves of the 5th May were 2—6 cm. long. The sap contained no oxalic acid or oxalate, but lime was readily detected; nitrates were absent. The ash contained carbonate, indicating the pre-existence of an organic acid.

Symphoricarpus.—The leaves (2nd May) were 6 cm. or less long. The sap gave an indistinct and doubtful reaction for nitrate with diphenylamine. Some leaves of the 6th May gave a deep-blue colour, whilst others of the same date gave a slight reaction. The sap contained no alkaline oxalate, whilst it is uncertain whether calcium oxalate was present or not. The analytical results are given in the table below, together with those obtained with *Cuscuta* and *Lathræa*.

Lathræa squamaria.—The sap gave no nitrate reaction, but reddened litmus. The ash of the stalk, treated with sulphuric acid, gave off much carbonic anhydride, and crystals of gypsum separated; no oxalate crystals could be detected. It is probable that the leaves contain traces of calcium oxalate, too minute to be weighed.

Cratægus oxyacantha.—The sap reddened litmus slightly. No

oxalic acid could be detected, but lime was found in considerable amount.

Juglans regia.—The sap reddened litmus. Calcium was found, but no oxalic acid.

Sambucus nigra.—All the leaves (5th May) gave blue coloration with diphenylamine sulphate. The ash contained calcium.

Aspidium filix mas.—A piece of a leaf stalk (0·5 cm.) gave only a trace of ash, which melted when heated on platinum. It contained only a trace of calcium, if any. Oxalic acid was absent, but it is probable that an alkaline organic salt was present.

Cuscuta europæa.—The sap reddened litmus; it contains no oxalic acid, but probably another organic acid and a trace of calcium. A large amount of substance was extracted, the solution evaporated, and the syrup treated with animal charcoal; after some weeks, crystals of oxalate could be detected with a microscope.

The following table gives the percentage amounts of soluble, insoluble, and total dry matter, the amounts of ash in the soluble and insoluble portions, and in total dry matter, and the percentage of lime in the ashes:—

	Dry matter.			Ash.			Lime in pure ash.		
	Soluble in water.	Insoluble in water.	Total.	In the soluble substance.	In the insoluble substance.	In total dry substance.	Of soluble substance.	Of insoluble substance.	Total ash.
Cuscuta europ...	4·4	6·43	—	11·0	3·31	5·07	2·7	6·01	2·94
Symphoricarpus racemosa	6·1	10·6	16·61	4·22	2·65	—	21·05	20·0	20·25
Lathræa squamaria	3·72	6·82	10·54	21·9	3·11	—	0·476	25·16	6·85
Do.	5·04	5·17	11·11	20·0	—	—	1·61	—	—
Do.	—	—	—	—	—	—	—	—	5·1
Do.	—	—	10·71	—	—	—	—	—	11·3

The results of the experiments show that calcium compounds are universally present in young spring leaves, so that the absence of oxalic acid is not due to absence of lime. The amount of lime varies considerably, and is partly in a soluble and partly in an insoluble form; the dissolved lime is perhaps in combination with an organic acid. Oxalic acid and alkaline oxalates could never be detected with certainty, and if present at all occur only in traces. Calcium oxalate could not be found in the cells, and only traces could be obtained by using large amounts of substance. It is thus seen that the change of substance of the cells does not necessarily yield oxalic acid even in presence of calcium salts; in the case of *Cuscuta* it was seen that the greater part of the bases existed as organic salts (not oxalates).

N. H. M.

The Latex of Ficus carica. By U. Mussi (*L'Orosi*, **14**, 297—304).—The latex of the common fig, *Ficus carica*, is a white, mobile liquid with a disagreeable odour, a bitter taste, and an acid reaction; its specific gravity is 1·05. If left in the dark without access of air, it slowly deposits small, white, amorphous masses of an elastic substance. When exposed to air and light, it darkens, and sometimes putrefies. It is composed of an enormous number of microscopic granules resembling in structure those of potato starch, but containing neither starch, inulin, nor nitrogenous compounds.

By filtration, the latex may be divided into a liquid and a solid portion. The former contains vegetable albumin, traces of mineral salts, substances of a gummy and pectic nature, among which occurs a new digestive ferment, termed by the author, *cradin*, and described in a previous paper (*L'Orosi*, **13**, 364), glucose, and malic acid. The solid portion consists of cerotic acid, caoutchouc, a white substance insoluble in water, but soluble in cold alcohol, ether, and chloroform, and a substance occurring in thin scales, insoluble in water and all ordinary solvents. The percentage composition of the latex is as follows:—

Cradin.	Albumin.	Gummy and peptic substances.	Resinous matters.	Extractive matters.	Insoluble organic compound.
6·89	3·51	0·07	1·53	1·23	2·43

Glucose.	Malic acid.	Cerotic acid.	Caoutchouc.	Water.	Ash.
1·29	0·47	2·79	12·86	66·19	0·76

S. B. A. A.

Cause of Acidity in Green Grapes. By C. Ordonneau (*Bull. Soc. Chim.* [3], **6**, 261—264).—See this vol., p. 589.

Constituents of the Nitrogen-free Extract. By W. E. Stone (*Chem. News*, **65**, 39—40).—The author has shown by means of the furfuraldehyde reaction, that many of our feeding-stuffs such as hay, straw, bran, maize, brewers' grains, &c., contain very appreciable quantities of gum-like carbohydrates which on hydrolysis yield pentoglucoses, or pentoses, arabinose, or xylose, as the case may be. These substances are practically insoluble in water, but may be extracted from tissues by heating with weak alkalis, and in the course of an ordinary fodder analysis they would count as carbohydrates. Their value as a food is, however, very doubtful, as the author has tested the excreta of animals for substances of this class with positive results. The manure of steers fed on a diet composed largely of maize ensilage yielded an amount of furfuraldehyde equivalent to more than 5 per cent. of these compounds. Owing to the incompleteness of the method by which they were obtained, the percentage found was no doubt considerably below the truth.

The author hopes to gain some light as to the absolute digestibility of these substances, and promises further experiments on the subject (compare this vol., p. 645). L. de K.

Truffles: Relation between the Terfâs or Kamés of Africa and Western Asia and the Truffles of Europe. By A. Chatin (*Compt. rend.*, **114**, 46—53).—The terfâs or kamés belong to the genus *Terfezia*, with the exception of one, *Tirmania Africana*. The soils in which they grow may be termed terfasseries.

Soils of the Terfasseries.

	I.	II.	IV.
Nitrogen	0·140	0·145	0·16
Phosphoric acid	0·151	0·170	0·20
Iodine	decided traces	decided traces	decided traces
Calcium oxide	10·420	4·240	7·50
Potassium oxide	0·295	0·264	0·35
Ferric oxide	3·019	1·077	2·90
Manganese dioxide	0·019	0 020	decided traces
Sulphuric acid	—	—	2·50
Chlorine	—	—	0·21
Magnesium oxide	—	—	0·40
Sodium oxide	—	—	0·08
Silica	—	—	75·60
Organic matter	—	—	8·60

Composition of the Tubercles.

	I.	II.	III.	IV.
Nitrogen	3·570	3·960	0·49	3·80
Organic and volatile matter	68·980	85·740	11·80	87·70
Ash	27·450	10·300	1·61	8·50
Water	—	—	86·10	—
	100·00	100·000	100·00	100·00

I, II, and IV were analysed after drying; No. III was analysed in the natural moist state. In some cases the proportion of ash is increased by the earthy matter that adheres tenaciously to the tubercle.

In the ash of No. I (see table on next page) the proportion of potash, phosphoric acid, &c., is reduced in consequence of the considerable admixture of earthy matter. I is the terfâs of Barika (*Terfezia Boudieri*). The soil is an ochre-coloured, pulverulent clay, containing numerous small fragments of calcium carbonate; II is the terfâs of Briska (*Tirmania Africana*); III is the kamé of Damas (*Terfezia Claveryi*); IV is the kamé of Bagdad (*Terfezia Hafazi*). The soil is a very fine clay, which effervesces strongly with acids.

The earth of the terfasseries is much more friable, and much lighter

Composition of the Ash of the Tubercles.

	I.	II.	III.	IV.
Phosphoric acid	5·390	12·330	13·40	15·60
Sulphuric acid	3·360	3·660	4·50	3·70
Chlorine	0·210	0·280	0·25	0·24
Iodine	decided traces	decided traces	traces	decided traces
Potassium oxide	3·930	9·800	8·18	11·10
Sodium oxide	0·670	2·810	1·70	2·20
Calcium oxide	6·560	3·200	19·10	7·20
Magnesium oxide	2·620	2·620	2·39	1·50
Ferric oxide	1·600	3·590	5·65	4·80
Manganese dioxide	0·005	0·005	0·04	decided traces
Silica	79·925	61·705	55·21	53·66
	100·000	100·000	100·00	100·00

than the earth of the truffle beds; it contains a considerable quantity of fragments of calcium carbonate. Iron, nitrogen, and phosphoric acid are present in both cases. Potash is present in considerably lower proportion in the earth of the terfasseries than in the earth of the truffle beds.

In general composition the terfâs are similar to truffles. The proportion of phosphoric acid, however, is only half as great in the former as in the latter. This is true also of potassium. Chlorine, iodine, sodium, calcium, magnesium, iron, and manganese are present in practically the same proportions in both cases.

Judging from their composition, the terfâs or kamés should constitute a valuable food. C. H. B.

Spontaneous Oxidation of Humic Acid and Vegetable Soil. By Berthelot and G. André (*Compt. rend.*, **114**, 41—43).—Humic acid from sugar and starch, when exposed to light in presence of air and moisture, changes to a yellow substance. A very small quantity of a soluble substance is formed at the same time. The humic acid is oxidised, and carbonic anhydride is evolved, but no nitrogen is oxidised during the change, and the alteration does not extend beyond the superficial layer. Humic acid extracted from soils by potash and precipitated by hydrochloric acid behaves in a similar manner, although the change takes place less rapidly, probably because the humic acid has previously been partially oxidised.

The change takes place in complete absence of bacteria, and hence the latter are not essential to the oxidation of the vegetable matter in soils, although they do in nature play an important part. The observation that humic acid is oxidised under the influence of light in presence of air and moisture explains why earth that is continually exposed gradually loses its organic matter. Since also it seems that the product of oxidation is more readily assimilated than the original

humic acid, the observation also explains why, within certain limits, free exposure of a vegetable soil to air and light increases its fertility.

C. H. B.

Estimation of Sulphur in Vegetable Soils, and the Forms in which it is Present. By Berthelot and André (*Compt. rend.*, **114**, 43—46).—The ratio of total sulphur to sulphur present as sulphates varies considerably in different soils, the organic sulphur being sometimes equal to, and sometimes much greater than, the sulphur as sulphates.

The total sulphur can only be estimated by complete destruction of the soil. Even chlorine in presence of hot aqueous potash is unable to effect complete oxidation. It is noteworthy, too, that 10 per cent. aqueous potash seems to be incapable of completely decomposing the calcium sulphate.

A point of great importance is the ratio of organic sulphur to organic nitrogen. In one case the sulphur was 8·7 per cent. of the nitrogen; in another it was 36·5 per cent. It would seem that in cases like the first the sulphur is present in a form similar to the proteïds, whilst in the others it is present in the form of carbon compounds of a very different character.

C. H. B.

Influence of the Proportion of Clay and Organic Nitrogen in Fallow Soils on the Absorption of Atmospheric Nitrogen, the Retention of Nitrogen, and Nitrification. By P. Pichard (*Compt. rend.*, **114**, 81—84).—In soils growing no crops, the absorption of atmospheric nitrogen is greatly accelerated by the presence of clay, and within certain limits the increase in nitrogen is proportional to the quantity of clay present. About 10 per cent. of the absorbed nitrogen is found in the form of nitrates, and 8 to 10 per cent. in the form of ammonium salts. The addition of calcium sulphate increases the quantity of nitrogen fixed, probably by preventing loss in the form of ammonium carbonate. The beneficial influence of clay is also observed in mixtures of clay, sand, and seed cake; addition of calcium sulphate reduces the loss of nitrogen in this case also, but addition of calcium carbonate increases it.

When soils contain 2—3 grams of organic nitrogen per kilo., the presence of clay prevents loss of nitrogen, but does not seem to facilitate its absorption.

For a given quantity of organic nitrogen, the presence of clay sometimes facilitates, and sometimes impedes, nitrification. With 1 gram of organic nitrogen per kilo., the presence of clay seems to be beneficial. Increase of organic nitrogen from 1 gram to 3 grams per kilo. is unfavourable to nitrification, seemingly because ammonium carbonate is formed more rapidly than it can be nitrified.

If it is desired to prepare a compost so that the nitrogen shall all be converted into nitrates, the quantity of organic nitrogen should not exceed 1 gram per kilo., and about 30 per cent. of clay and 0·5 per cent. of calcium sulphate should be added. For an ammoniacal compost, the proportion of organic nitrogen should be increased to 2 or 3 grams per kilo., and clay and calcium sulphate may be added with advantage. In soils where cessation of nitrification seems to be

due to the formation of too much ammonia, calcium carbonate should be added. C. H. B.

Analytical Chemistry.

New Drying Apparatus for Elementary Analysis. By E. Sauer (*Ber.*, **25**, 258).—The author describes a form of drying apparatus for use in elementary analysis; it consists of two wash-bottles, made entirely of glass, and containing concentrated potash; two others, containing concentrated sulphuric acid; and two large U-tubes, provided with lateral tubulures, and partly filled with granulated calcium chloride, and partly with soda-lime. The air or oxygen is passed through one-half of the apparatus in the usual way, and, as only four corks are used in the construction of the apparatus, it is easily kept air-tight if the india-rubber tubing which forms the connections is occasionally renewed. F. S. K.

Estimation of Iodates in Potassium Iodide. By T. Gigli (*L'Orosi*, **14**, 229—232).—4 to 5 grams of potassium iodide is dissolved in 300 c.c. of distilled water, 20 c.c. of dilute sulphuric acid (2 per cent.) added, and the iodine liberated ($5HI + HIO_3 = 3H_2O + 3I_2$) titrated with decinormal sodium thiosulphate and starch. 1 molecule of sodium thiosulphate corresponds with 1 atom of iodine, and hence with $\frac{1}{6}$ mol. KIO_3. The reaction which occurs is represented by the equation $2Na_2S_2O_3,5H_2O + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O$, no secondary reactions being introduced by the presence of sulphuric acid in the solution. S. B. A. A.

Influence of Temperature on Griess' Reaction for Nitrites in Water. By G. Bosio (*L'Orosi*, **14**, 416—418).—The temperature at which Griess' test for nitrites is carried out has a considerable influence on the time required for the appearance of the coloration, and on the depth of the tint. When, for instance, it is applied to water at a low temperature (0° to 10°) the product is insoluble, and separates as a reddish-white, gelatinous precipitate, which, on raising the temperature to 40—50°, redissolves instantaneously, giving the characteristic crimson coloration. To obtain accurate and comparable results when the reaction is used for colorimetric determinations, it is advisable to uniformly heat the water to the boiling point, or to 50—60°, after adding the reagents. S. B. A. A.

Estimation of Sulphur in Inorganic Sulphides. Analysis of Molybdenite, Realgar, and Orpiment. By P. Jannasch and V. Wasowicz (*J. pr. Chem.* [2], **45**, 94—102).—The method is based on the volatilisation of the sulphur as oxides into a solution of hydrogen peroxide, when it is completely converted into sulphuric acid. The finely powdered mineral, contained in a platinum boat, is heated

at a red heat in a stream of oxygen, and the gaseous products passed into three cylinders containing 3 per cent. hydrogen peroxide free from sulphuric acid. About 150 c.c. of hydrogen peroxide is required, and the heating takes about $1\frac{1}{2}$ hours, and must not be too strong, or molybdic anhydride is sublimed. When the heating is ended, the boat with its contents is drawn out of the tube with a wire and weighed. The residue is then heated in a covered porcelain dish with ammonia on the water-bath for an hour, and the insoluble residue collected and washed with ammonia, and then with ammonia and water. The filtrate is heated on the water-bath to get rid of ammonia, and precipitated with mercuric nitrate. After 24 hours, the mercury molybdate is collected, washed with dilute mercuric nitrate, dried at 110°, separated from the filter-paper, the latter carefully washed with dilute nitric acid, the washings evaporated in a weighed Rose's crucible, the precipitate then added, and the whole reduced to metallic molybdenum in a stream of hydrogen.

The residue insoluble in ammonia is extracted with hydrochloric acid, and the iron determined in the solution by precipitation with ammonia. In the sample employed, the insoluble gangue still remaining was chiefly quartz, and amounted to 3·38 per cent.

To determine the sulphur, the hydrogen peroxide solution and the combustion tube are rinsed into a porcelain dish, the liquid evaporated to about 100 c.c., mixed with 2 c.c. of dilute hydrochloric acid, and precipitated boiling with barium chloride. The water in the mineral was determined by drying it over phosphoric anhydride for 48 hours. The results obtained are good.

Realgar and orpiment are both easily decomposed by heating in a current of oxygen. The residue in the boat amounted to 0·2—0·3 per cent. in the case of the realgar, and 0·5—0·6 per cent. in the case of the orpiment employed. The hydrogen peroxide solution is evaporated on the water-bath to 140 c.c., mixed with excess of ammonia, and the cold solution precipitated with magnesia mixture. After 24 hours, the precipitate is collected, washed with ammonia, dissolved in hydrochloric acid, and reprecipitated with ammonia, with the addition of a few drops of magnesia mixture. The precipitate dried at 100° is separated from the filter, the latter extracted with dilute nitric acid, the solution evaporated in a weighed Rose's crucible, then the precipitate added, and gradually heated in a current of oxygen, and weighed.

The sulphuric acid is determined in the filtrate, after evaporating off the ammonia in the usual way.

The author also discusses the question of priority as regards the above method. E. C. R.

Estimation of Sulphur in Galena and Minerals containing Lead. By P. Jannasch and K. Aschoff (*J. pr. Chem.* [2], **45**, 103—109).—The method depends on oxidising the mineral at a red heat by means of a current of oxygen saturated with vapours of nitric acid, and then volatilising the sulphuric acid so formed, with the aid of ammonium carbonate, into receivers containing hydrogen peroxide.

About 0·4 gram of galena in very fine powder is weighed into a porcelain boat, and heated at a dull red heat in a somewhat brisk current of oxygen and nitric acid vapour. After 20 minutes, the heat is raised and maintained for an hour; the oxygen is then replaced by air, and finally a current of air saturated with ammonium carbonate is passed through the tube; in about half an hour, the contents of the boat begin to melt and froth slightly, and the substance then becomes bright yellow, which is a sign that the reaction is finished. The boat is then drawn out of the tube, and the contents of the receivers and the tube washed into a porcelain dish, evaporated to about 100 c.c., and the sulphuric acid precipitated with barium chloride. The method gives accurate results.

The details of an analysis of bournonite by this method are also given. E. C. R.

Estimation of Sulphur in Vegetable Soils. By Berthelot and André (*Compt. rend.*, **114**, 43—46; compare this vol., p. 656).

Rapid Estimation of Sulphuric Acid. By P. Cazeneuve and Nicolle (*J. Pharm.* [5], **25**, 51—53).—Artificial seltzer water may contain occasionally as much as 0·50 gram of free sulphuric acid per litre, due to the method of manufacture. This may be approximately estimated, without titrated solutions, by the use of saturated lime-water charged with excess of carbonic anhydride. In preparing this solution, the first and second portions of water are rejected as possibly containing potash. Such a solution contains about 1·29 grams of CaO per litre, and 1 c.c. represents 0·0022 gram of sulphuric acid. To apply the process, 1 c.c. of the solution is placed in each of five test-tubes, then 4 c.c. of the mineral water to be examined is placed in the first one, 8 c.c. in the second, 12 c.c. in the third, &c. The five tubes are boiled, and if all become turbid, the amount of sulphuric acid may be neglected. If, for example, the second tube becomes turbid but the third one is clear, this serves as a first approximation, and four more tubes are charged with 8 c.c., 9 c.c., &c., and boiled. If now the tube containing 9 c.c. of mineral water becomes turbid, but the one containing 10 c.c. is clear, the latter tube then contains approximately 0·0022 gram of sulphuric acid, and a litre contains 0·22 gram. The process is only good in certain cases, but it frequently affords useful information. J. T.

Analysis of "Karlsbad Salts." By W. Kubel (*Arch. Pharm.*, **229**, 588—590).—In order to test the quality of "Karlsbad salts," which is now a recognised medicine in Germany, the author recommends that the specific gravity of a solution of 25 grams of the anhydrous salt, or 45 grams of the hydrated salt in 200 c.c., and the percentages of chlorine and alkali, the latter calculated as sodium hydrogen carbonate, should be determined. The salt should consist of crystallised sodium sulphate, 55·55 per cent.; potassium sulphate, 1·11; sodium chloride, 10; sodium hydrogen carbonate, 33·33 per cent. The specific gravity of the solution of 25 or 45 grams respectively in 200 c.c. of water should be 1·1037 at 15°. J. W. L.

Analysis of the Barium Group. By W. Fileti (*Gazzetta*, **21**, ii, 365—378).—In view of the recent work of Schweitzer, Fresenius, and Lüdeking (Abstr., 1890, 826, 924; and 1891, 110, 364), &c., the author has re-examined the behaviour of the metals of the barium group with especial reference to their qualitative separation.

Hydrofluosilicic Acid.—With this reagent, a 0·05 per cent. solution of barium chloride becomes turbid in 15 minutes, and a precipitate is gradually formed; a 0·025 per cent. solution is precipitated on the addition of half its volume of alcohol. A 3 per cent. strontium chloride solution is precipitated in 15 minutes on the addition of an equal volume of alcohol; a 6 per cent. solution is similarly precipitated on adding half its volume of alcohol. Calcium salts give precipitates with hydrofluosilicic acid and alcohol, which redissolve in excess of the acid. A 0·05 per cent. solution of barium chloride, containing 30 times as much strontium chloride, is readily precipitated by hydrofluosilicic acid on adding half its volume of alcohol; a 0·1 per cent. solution of barium chloride, containing 30 times as much strontium chloride and no alcohol, only gives a slight precipitate after long standing, and the amount of precipitate diminishes as the proportion of strontium chloride is increased. A 0·1 per cent. solution of barium chloride, containing 40 times as much calcium chloride, is barely precipitated by hydrofluosilicic acid after the addition of half its volume of alcohol. It thus appears that salts of strontium or calcium prevent or retard the precipitation of small quantities of barium by hydrofluosilicic acid.

Chromic Acid.—Neutral or ammoniacal 6 per cent. solutions of strontium chloride are immediately precipitated by potassium chromate in the cold; the precipitation is more complete on heating, and, contrary to Lüdeking's statement, there is also a precipitate in acetic acid solutions in presence of sodium acetate, especially on heating. A 2 per cent. neutral or ammoniacal solution of strontium chloride is slowly precipitated by potassium chromate in the cold; in presence of sodium acetate and acetic acid there is an immediate turbidity if there is an excess of chromate; 1 per cent. solutions are more slowly precipitated in the cold, but even solutions strongly acidified with acetic acid are at once precipitated in presence of an excess of potassium chromate. 0·002 per cent. solutions of barium chloride become turbid on the addition of potassium chromate, an excess of which must be added if an ammoniacal salt or acetic acid is present. Solutions of strontium chromate precipitate 0·004 per cent. solutions of barium chloride, but ammonium salts and free acetic acid prevent the precipitation of small quantities of barium. The presence of strontium and calcium chlorides interferes very little with the precipitation of barium by potassium chromate, but prevents its precipitation in small quantities by strontium chromate. A 0·004 per cent. solution of barium chloride, containing 300 times as much strontium chloride or 2000 to 4000 times as much calcium chloride, is readily precipitated by potassium chromate. With strontium chromate, a clear reaction cannot be obtained with a solution of barium chloride more dilute than 0·02 per cent. in presence of

60 times as much strontium chloride, or 100 parts of calcium chloride. The barium reaction with potassium or strontium chromate is thus more sensitive than that with hydrofluosilicic acid; the reaction with potassium chromate is not affected by the presence of acetic acid or ammoniacal salts, provided the reagent is added in excess, whereas the action of strontium chromate is impeded. In testing for barium, potassium chromate should therefore be added in the cold, the solution being made so dilute as to contain less than 0·5 per cent. of strontium salts. If strontium chromate is used, the solution should be made neutral or ammoniacal, or, if possible, entirely freed from ammonium salts.

The presence of calcium renders the detection of small quantities of strontium difficult. Lüdeking has shown that in presence of much calcium considerable quantities of strontium may be present without any precipitate being given by calcium sulphate. Sidersky's methods (Abstr., 1883, 508) of precipitating an ammoniacal solution of calcium and strontium with a mixture of ammonium sulphate and oxalate, and dissolving out the calcium oxalate from the precipitate with hydrochloric acid, or of directly precipitating the strontium by the same reagents in an hydrochloric acid solution, have been shown by Russmann (Abstr., 1891, 111) and by the author's experiments to be useless for the detection of small quantities of strontium.

Potassium Ferrocyanide.—On adding a large excess of a saturated solution of this reagent to a solution of calcium chloride made alkaline with ammonia, and boiling for a few minutes, the solution only retains traces of calcium. The precipitation is more complete in presence of ammonium chloride, but this acts on the ferrocyanide, forming an insoluble compound, which passes through the filter paper. To obtain a complete precipitation of the calcium, the solution is treated with excess of ammonium chloride and much ammonia, heated to boiling, an equal volume of a saturated solution of potassium ferrocyanide added, the whole boiled for a short time, allowed to remain for 15 minutes, and filtered; the filtrate is again tested in the same way.

A boiling 5 per cent. solution of barium chloride is incompletely precipitated by potassium ferrocyanide; a 2 per cent. solution only after some time; more dilute solutions are not precipitated at all. Solutions of strontium chloride are not precipitated at all by potassium ferrocyanide. The presence of several metals of the group together in solution does not sensibly affect their reactions; thus 0·0003 gram of barium chloride may be detected in presence of 0·10 gram of calcium chloride, and 0·003 gram of strontium chloride may be detected in presence of 0·20 gram of calcium chloride.

From the above experiments, the following method for the qualitative analysis of the group is deduced. The mixed carbonates, after washing, are suspended in water, heated to boiling, dissolved in dilute acetic acid, the carbonic anhydride boiled off, one portion tested for barium with strontium or potassium chromate, another portion is freed from barium and strontium by sulphuric acid and tested for calcium with ammonium oxalate and ammonia.

Calcium Absent.—Barium, if present, is removed with potassium

chromate in alkaline solution, and strontium is precipitated by adding sulphuric acid to the filtrate.

Calcium Present.—The solution is made alkaline with ammonia, heated, an equal volume of a saturated solution of potassium ferrocyanide added, and the whole boiled for a few minutes and filtered. The filtrate, after being tested for calcium, may be examined in two ways: 1st. Barium is precipitated by potassium chromate in the cold, and the filtrate tested for strontium by boiling with potassium sulphate. 2nd. Barium and strontium are precipitated together in the cold with dilute sulphuric acid, and the mixed sulphates boiled with potassium carbonate and sulphate, &c. S. B. A. A.

Estimation of Silver and Gold by means of Hydroxylamine Hydrochloride. By A. Lainer (*Monatsh.*, **12**, 639—641).—Hydroxylamine hydrochloride, in presence of potassium or sodium hydroxide, may be conveniently used for the estimation of silver in silver nitrate, silver sodium thiosulphate, and potassium silver cyanide, as well as for the complete reduction of silver chloride, silver bromide, and silver iodide. The presence of organic acids, such as citric acid, in no way interferes with the estimation of silver by this method.

In the estimation of silver, in solutions containing other metals, for example, copper, it is first precipitated as chloride, and the washed precipitate then reduced by boiling it with an aqueous solution of hydroxylamine hydrochloride and potassium hydroxide.

When hydroxylamine hydrochloride is added to a cold solution of auric chloride, the metal is only slowly precipitated, but on warming, the reduction soon becomes complete. This reaction may with advantage be employed in separating gold from solutions containing the chlorides of the alkalis and alkaline earths, as it gives accurate results. Gold is not precipitated by hydroxylamine hydrochloride when the solution contains an alkaline cyanide; the presence of sodium thiosulphate does not, however, prevent the reduction. In conclusion, the author suggests that hydroxylamine hydrochloride may be usefully employed in recovering gold and silver from photographic residues. G. T. M.

Analysis of Galena. By P. Jannasch and K. Aschoff (*J. pr. Chem.* [2], **45**, 110—111).—The galena is decomposed with strong nitric acid in a large porcelain crucible, the precipitated sulphur oxidised with bromine, and the mixture evaporated to dryness. The residue is then mixed with water, the lead sulphate brought into solution with excess of pure sodium hydroxide, diluted with water, filtered from gangue, and the solution mixed in a deep porcelain dish with bromine, and, after some time, heated on the water-bath until all the bromine has passed off. The precipitated lead oxide is filtered and washed with a very dilute solution of sodium chloride (if pure water be used for washing, the precipitate goes through the filter). The filtrate is acidified with hydrochloric acid, evaporated to dryness, taken up with water and 2 c.c. hydrochloric acid, and the sulphuric acid precipitated with barium chloride.

The lead is determined by dissolving it in nitric acid, and precipitating as sulphate. E. C. R.

Analysis of Galena by Precipitation of the Lead with Hydrogen Peroxide in Ammoniacal Solution. By P. Jannasch and T. Bickes (*J. pr Chem.* [2], **45**, 111—113).—0·5 gram of the finely-powdered mineral is decomposed with fuming nitric acid, the precipitated sulphur oxidised with bromine, and the mixture evaporated to dryness three or four times with concentrated hydrochloric acid. The lead sulphate is then dissolved in 10 c.c. of ammonia, 10 c.c. of acetic acid, and water, and the solution warmed on the water-bath and filtered from a small quantity of gangue. The cold filtrate is mixed with 60 c.c. of a mixture of equal volumes of concentrated ammonia and hydrogen peroxide, 60 c.c. more of hydrogen peroxide added, and then small quantities of the precipitant until the settled mixture gives no turbidity on a further addition. The mixture is allowed to remain an hour with frequent shaking, and the precipitate collected and washed with cold water. The lead and sulphuric acid are then determined in the usual way.

It is necessary that the precipitation of the lead by hydrogen peroxide be conducted in the cold, since the action of hydrogen peroxide goes further when warmed, and the reddish-yellow precipitate is converted into a white compound. The latter is partially soluble in hot water, and crystallises in lustrous leaflets. E. C. R.

Analysis of Galena by Heating it in a Stream of Air saturated with Bromine. By P. Jannasch and T. Bickes (*J. pr. Chem.* [2], **45**, 113—114).—The authors find that a mixture of oxygen and bromine vapour acts very readily on natural lead sulphide. The sulphur is carried over as sulphur bromide, and lead bromide remains behind. The sulphur is determined as described in the preceding abstracts. The lead bromide is treated with chlorine-water, dissolved in nitric acid, the solution filtered from gangue, and the lead precipitated as sulphate. E. C. R.

Volumetric Estimation of Mercury. By R. Namias (*Gazzetta*, **21**, ii, 361—364).—This method is based on the action of stannous chloride on an acid solution of mercuric chloride, which takes place, as is well known, in two stages, in which mercurous chloride and mercury are respectively obtained. Whilst, however, the first reaction occurs instantaneously, the second only takes place after an interval, the length of which depends on the excess of stannous chloride present. On placing a drop of the solution on filter paper moistened with sodium molybdate, a slight excess of stannous chloride gives a bluish stain.

In practice, compounds of mercury are first converted into mercuric chloride, and the solution of stannous chloride standardised, first approximately with iodine and then with pure sublimed mercuric chloride; the sample is then titrated under the same conditions as the standard. S. B. A. A.

Analysis of Chrome Yellows. By Lachaud and Lepierre (*Bull. Soc. Chim.* [3], **6**, 235—237).—The authors make use of the

fact that dilute potassium hydroxide solution dissolves lead chromate with formation of a basic lead chromate and of potassium chromate according to the equation

$$2PbCrO_4 + 2KHO = PbCrO_4,PbO + K_2CrO_4 + H_2O.$$

Under definite conditions, the potassium hydroxide which does not enter into the reaction may be determined, and the lead chromate present is deducible from this. The method of operation is as follows:—2 grams of the lead chromate are well shaken with binormal potassium hydroxide solution (20 c.c.) until the lead chromate is decomposed; after dilution with distilled water, the alkaline solution is decanted from the basic chromate and titrated with normal sulphuric acid, using phenolphthaleïn as an indicator. T. G. N.

Decomposition of Minerals containing Titanium. By J. Jones (*Chem. News*, **65**, 8).—The author recommends the following process:—2 grams of the mineral is placed in a pressure bottle with 20 c.c. of water and 20 c.c. of sulphuric acid, and the bottle is then put for two hours in an air-bath, the temperature of which is raised to 200°. The residue will consist of practically pure silica, whilst the titanium and other refractory bases pass into solution. If a pressure bottle is not at hand, one can easily be improvised. The author found an old bromine bottle to be sufficiently strong. L. de K.

Colour Reactions of Carbohydrates. By G. Bertrand (*Bull. Soc. Chim.* [3], **6**, 259—261).—On gently warming a glucose with concentrated hydrochloric acid (sp. gr. 1·18) to which traces of phloroglucinol have been added, a yellow coloration is developed which, passing to orange, is thrown down as a dirty-red precipitate on further heating, while the supernatant liquid becomes colourless. The reaction also takes place in the cold after many hours. Orcinol may be substituted for phloroglucinol in the above experiment, and definite colours are obtained with carbohydrates as under:—

1. *Orange-red.*—Glucose (Soxhlet's), glucose (from cellulose), galactose, mannose, levulose, sorbose, saccharose, lactose, maltose, raffinose, melezitose, stachyose, trehalose, isodulcitol, glycogen, inulin, starch, dextrin, achroodextrin, amygdalin, salicin, hesperidin.

2. *Violet-blue.*—Arabinose, xylose, cherry-gum, and pine-gum, whilst gum arabic and Senegal gum afford a violet-red color.

3. No coloration is yielded by xylite, sorbitol, dulcitol, mannitol, perseïtol, inosite, pinite, bergenite, or saccharin.

The author states that this coloration is due to the generation of furfuraldehyde derivatives in the course of the reaction, since furfuraldehyde behaves like the C_5 sugars, and methylfurfuraldehyde like the C_6 sugars in respect to the coloration produced, whereas the mannitols, which are unable, under the conditions of experiment, to produce furfuraldehyde compounds, give no colour. T. G. N.

Iodine Number for Lard Oil by the Hübl Method. By R. Haines (*Chem. News.*, **65**, 39).—The author carefully prepared several samples of lard oil, and took their iodine absorption by Hübl's method. The purest medicinal chloroform was used, and the iodine

reagent was allowed to act for at least three hours. All the experiments were made under exactly the same conditions, particular attention being paid to the temperature; it was found that the iodine absorption varied from 70·01° to 75·14°.

A peculiar fact, which the author is unable to explain, is that a sample of country lard of low melting point, and also the lard oil prepared from it, gave lower iodine numbers than the more solid lards and the oils made from them. L. DE K.

Rapid Method of Determining the Composition of Lubricating Oils. By H. GRIPPER (*Chem. News*, **65**, 27—28).—The author proposes the following process, which, although it only gives results within 2 or 3 per cent. of the truth, is very useful for technical or commercial purposes on account of its simplicity and rapidity. The method is simply an extension of the well-known Koettstorfer process. 2·5 grams of the sample is saponified as usual with 25 c.c. of N/2 alcoholic potash, and the excess of this is titrated back with N/2 hydrochloric acid, using phenolphthaleïn as indicator. Assuming the fatty matter to consist of brown cotton-seed oil, brown rape-seed oil, neatsfoot oil, lard oil, tallow oil, or castor oil, or their mixture, its absorption may be taken at 20·08 per cent. The percentage of potash absorbed by the sample multiplied by 4·98 will therefore represent the percentage by weight of fatty oil in the mixture.

If the amount by volume is required, it is necessary to take the sp. gr. not only of the sample but also of the unsaponifiable oil. In order to determine this, the liquid in the oil-flask is again heated to boiling, and poured through a filter moistened with boiling water. The soap solution rapidly runs through, whilst the mineral oil remains on the filter. Its sp. gr. is then taken by Hager's spirit method. L. DE K.

Analysis of White Wax. By G. BUCHNER (*Chem. Zeit.*, **14**, 1707).—The author has, a few years ago, called attention to the fact that a genuine sample of white wax may show an abnormally high saponification or acidity number if it has been bleached by chemical means. Analysts should, therefore, well consider this before pronouncing an opinion. The author's statement has been doubted, and it has been hinted that he was not supplied with genuine samples, but experiments conducted by Buisine prove him to be in the right. The acidity and saponification numbers may, in fact, come respectively as high as 24 and 100. L. DE K.

Detection of Quinine and Phenacetin in Urine. By F. SESTINI and R. CAMPANI (*L'Orosi*, **14**, 304—306).—From medico-legal investigations conducted by the authors they have arrived at the following conclusions:—The presence of phenacetin conceals the fluorescence of sulphuric acid solutions of the cinchona alkaloïds, especially when dilute. Aqueous solutions of phenacetin are coloured violet-yellow on the addition of chlorine-water and ammonia, but mixtures of quinine and phenacetin are coloured light-blue (methylene blue). Solutions of quinine acquire the characteristic green colour on

treatment with bromine vapour and a few drops of ammonia, even in presence of phenacetin, but no reaction is obtained if the solution is strongly acid. Very dilute solutions of quinine are coloured yellow by bromine vapour alone, even in presence of phenacetin; concentrated solutions give, with excess of bromine vapour or with bromine-water, a yellow precipitate which disappears on adding ammonia, without any green coloration being produced.

To obtain the green coloration of quinine salts with bromine, it is best to agitate the solution with bromine vapour until it becomes slightly turbid, and then add ammonia drop by drop; if there is much phenacetin present, the green coloration will be darker and have a violet tinge. On shaking it with ether, and allowing it to remain for a time, the lower layer assumes the emerald-green colour due to quinine, and the upper layer the violet-yellow of the phenacetin.

To detect quinine in the ethereal residues from urine or viscera examined by the Stas-Otto method, they are treated with ether, and the solution divided into two parts; to one of these, bromine vapour is added until a yellow precipitate begins to form, and then, on adding ammonia, the green colour slowly appears at the bottom of the tube. To the other portion, a saturated solution of bromine-water is added until the yellow precipitate of bromoquinine is thrown down, and this should be readily redissolved by ammonia. S. B. A. A.

Detection and Estimation of Santonine. By M. H. Manseau (*Chem. Centr.*, 1891, ii, 733—734; from *Rep. de Pharm.*, 1891, Nos. 1 and 2).—In cases of poisoning with santonine, the urine is evaporated to a syrup, treated with chloroform, the extract filtered, concentrated at a low temperature, and to the residue is added four or five drops of soda solution, together with a little alcohol. In the presence of santonine, a brick-red or blood-red coloration is formed when this solution is evaporated.

For the estimation of the alkaloïd in the seeds of *Artemisia santonica*, the drug is finely ground, mixed with calcium hydroxide, the mass extracted with alcohol, the latter distilled off, and the residue neutralised with hydrochloric acid. The tarry mass is then dissolved in 300 c.c. of alcohol (sp. gr. 0·935), treated with an excess of lead acetate, and the mixture heated for one hour at 60—70°. The precipitate is filtered off, washed with warm alcohol (in which the lead santonate is soluble), the lead precipitated as carbonate by the addition of sodium carbonate, the solution filtered, neutralised with hydrochloric acid, and the santonine weighed on a tared filter.

From pills, the alkaloïd may be extracted by chloroform, and weighed after distilling off the solvent. The author's results are, however, not quite exact. J. W. L.

Estimation of Free Alkaloïds and their Molecular Weight. By A. Christensen (*Chem. Zeit.*, **14**, 1346—1352).—Since Kjeldahl has called attention to the iodometric estimation of acids and alkalis as being particularly suitable for the determination of ammonia, the author has successfully applied the process to alkaloïds. The alkaloïd

is dissolved in a known excess of N/10 sulphuric acid, diluted with water up to 50 c.c., and, to prevent precipitation of iodised products, further mixed with 50 c.c. of spirit. An excess of potassium iodide (1—15), and then an excess of potassium iodate (1—25), is now added, and the liberated iodine just bleached by careful addition of N/10 sodium thiosulphate. If the amount of alkaloïd is unknown, it may be calculated by using the equation—

$$x = \frac{V(A - a)}{10{,}000}.$$

A = c.c. of sulphuric acid added; a = c.c. of thiosulphate; V = molecular weight of the alkaloïd.

If, on the other hand, the amount of alkaloïd taken is exactly known, but its molecular weight is required, the equation will be—

$$V = \frac{x.\ 100000}{(A - a)}.$$

The author strongly advises, if possible, not to work on too small quantities of the alkaloïd. The process is successful with all natural alkaloïds, with the exception of pilocarpine and narcotine, but altogether useless with theobromine and caffeïne, which substances can, however, scarcely be classed among the true alkaloïds. The process is no doubt of great interest to those engaged in the assay of opium. It is well known that the percentage of morphine in Persian opium is generally found somewhat too high, on account of co-precipitated foreign matters. If, however, the crude morphine is dissolved in sulphuric acid and then treated as described, very accurate results will be obtained. L. DE K.

Löwenthal's Method of Tannin Analysis. By R. L. WHITELEY and J. T. WOOD (*J. Soc. Chem. Ind.*, **10**, 523).—The authors find that in estimating small quantities of tannin matters, Löwenthal's method gives defective results. D. B.

Detection of Albumin in Urine. By P. CROCCO (*L'Orosi*, **14**, 372—379).—The author has found that the urine excreted in certain forms of liver disease, when tested by ordinary methods, gives precipitates which may be mistaken for albumin, but in reality consist of bile pigments, more particularly biliverdin. On treating such urine with acetic acid, a turbidity or precipitate either forms in the cold or on gently warming at a temperature insufficient to precipitate albumin. The precipitate is likewise thrown down by quantities of mineral acids too small to affect albumin; it is soluble in alcohol, and does not give the biuret reaction. To avoid error, it is sufficient to treat the urine with 2 to 3 per cent. of concentrated acetic acid, leave it in the cold for a few hours, and filter before applying the ordinary tests. S. B. A. A.

Detection of Vegetable Fibre in Silk or Woollen Tissue. By S. FURBINO (*L'Orosi*, **14**, 234—235; from *Il Selmi*).—This method

depends on the conversion of cellulose by concentrated sulphuric acid into dextrin and glucose, and on the reduction and decolorisation of colouring matters derived from archil in presence of glucose and alkalis, the original colour being restored by exposure to the air or by oxidation. The process is as follows:—A piece of the material about 1 sq. cm. in area is allowed to soak in a few drops of sulphuric acid (66°) for 5—10 minutes, water is added, the whole heated to boiling, the liquid decanted and made strongly alkaline with a concentrated solution of soda; a few drops of a very dilute solution of archil are then added, and the violet liquid obtained heated for a few minutes to about 90°. In presence of even small quantities of vegetable fibre (1 per cent. of cotton, flax, &c.), the colour of the solution is discharged; it may be restored by exposing the solution to the air in a shallow vessel. If the violet colour persists after heating for five minutes, the material can only contain an inappreciable amount of vegetable fibre. Before testing, care must be taken to cleanse the material from starchy matter, and other substances applied to it in the course of manufacture, by repeatedly boiling it with water, &c. S. B. A. A.

Valuation of Coal for Use in Steam Boilers. By T. T. P. B. Warren (*Chem. News*, **69**, 299).—The author suggests the estimation of the chlorine in the feed-water and in the boiler at certain intervals, as a measure of the water evaporated. During the tests any disturbing influences, such as priming, loss of chlorine, opening furnace doors, &c., must be avoided, and the boiler should be filled with fresh water to start with. The relationship of the data obtained to the result required are, $\left(\frac{C'}{C} \times G\right) - G =$ number of gallons evaporated, when C′ is the chlorine after some hours run, C the chlorine in the feed-water, and G the number of gallons in the boiler to the working level. It is suggested that a similar result may be obtained by taking the density, with a trustworthy hydrometer, instead of estimating the chlorine; then the number of gallons evaporated $= \left(\frac{D' - 1}{D - 1} \times G\right) - G$ in which 1 = specific gravity of pure water, G the same as in the above formula, whilst D, the initial density, is found by boiling some of the water, so as to throw out of solution any substances that would be precipitated in the boiler, and making up with distilled water the loss by evaporation; D′ is the density after some hours' run. D. A. L.

General and Physical Chemistry.

Relations between Compressibility and Indices of Refraction of Liquids. By G. Quincke (*Ann. Phys. Chem.* [2], **44**, 774—777).—The author has, from former experiments, deduced the relation $(n - 1)/\sigma = \text{const.}$, where n is the specific refraction, and σ the specific gravity of a liquid. The accuracy of this relation, and of the author's experimental results, has been placed in question by Röntgen. In the present paper, the author shows that his results agree better with those of other observers than do those of Röntgen.

H. C.

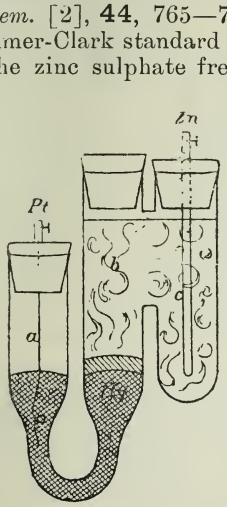
Rotatory Power of Diacetyltartaric Derivatives. By J. A. Le Bel (*Compt. rend.*, **114**, 304—306).—A discussion with Colson. The author points out that the idea that the radicles united with an asymmetrical carbon atom have their centres of gravity situated at the solid angles of a tetrahedron, with the carbon atom at its centre, is not an essential part of his theory of optical activity. The view is quite untenable in the case of closed chain compounds.

C. H. B.

Stereochemistry of Diacetyltartaric Acid; a Reply to Le Bel. By A. Colson (*Compt. rend.*, **114**, 417—419).—A continuation of the discussion as to the exact mode of the distribution of the radicles round an asymmetrical carbon atom (preceding abstract). The author considers that unless the radicles are supposed to occupy the summits of a *regular* tetrahedron, the hypothesis no longer has a definite character.

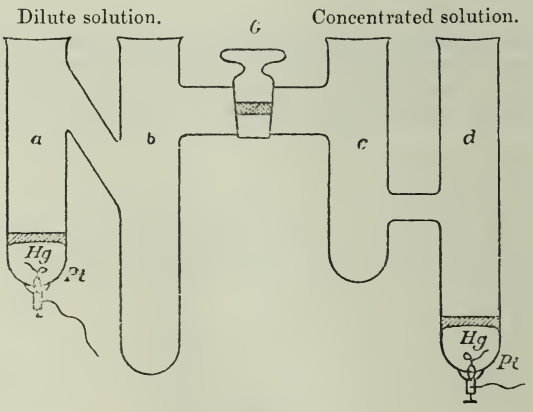
C. H. B.

Practical Form of the Latimer-Clark Standard Cell. By W. Negbaur (*Ann. Phys. Chem.* [2], **44**, 765—766).—Objections to the ordinary form of the Latimer-Clark standard cell are the presence of a porous pot, on which the zinc sulphate frequently is deposited in



crystalline form, and the necessity for using a somewhat large quantity of mercury, in order that when the cell is disturbed the end of the platinum wire immersed in the mercury may not become coated with mercurous sulphate. These objections are avoided by making use of a cell of the form given in the accompanying diagram. The height of the cell is 6 cm. The mercury is contained in the U-tube *ab*, into the shorter limb *a* of which passes the platinum wire, the longer limb *b* containing the mercurous sulphate paste. The cylindrical side tube *c* contains the zinc rod. The opening between *b* and *c* should be as large as possible. Crystallisation of the zinc sulphate can be avoided by covering the solution with a thin layer of vaselin. The cell should be protected from the action of light by coating it with black paper. The internal resistance is somewhat larger than that of the cell in its older form. H. C.

Standard Cell for Small Differences of Potential. By W. Negbaur (*Ann. Phys. Chem.* [2], **44**, 767—770).—No standard cell for use in the measurement of small potential differences has hitherto been described. The author advocates the use of cells formed of two solutions of the same salt or acid of different concentration, between mercury electrodes coated with calomel. The substances used can be readily obtained in a pure condition, and the potential difference may be altered within wide limits by altering the concentration of the solutions; moreover, this can be calculated beforehand, if necessary. A useful form of such a cell is that given in the figure. The glass tap G serves to separate the two solutions from one another, the bore of the tap containing a plug of parchment paper. The concentrated solution is placed in the apparatus to the right of the tap. The vessels *a* and *d*



contain the mercury coated with calomel paste. As it is only necessary to retain the original concentrations at the electrodes, the vessels *b* and *c* provide for overflow of either solution: in these also may be placed the thermometer. Platinum wires are sealed into *a* and *d* communicating with the mercury. Hydrochloric acid and sodium

or lithium chlorides are suitable for establishing the concentration current, the first being the best. A potential difference of 0·1 volt may be obtained by solutions containing 4 and 0·99 grams of hydrogen chloride, or 2·5 and 0·1 grams of sodium chloride per litre. The potential difference of a cell containing such solutions of hydrochloric acid was found to remain perfectly constant for eight days.

H. C.

Potential Differences at the Surfaces of Contact of very Dilute Solutions. By W. Negbaur (*Ann. Phys. Chem.* [2], **44**, 737—758).—The main object of the present paper was to obtain experimental confirmation of the theoretical deductions of Planck with regard to the difference of potential between two dilute solutions of electrolytes (Abstr., 1890, 1355). The observed values agree generally with those calculated by means of Planck's formula. In solutions of equivalent or nearly equivalent strength, the direction of the current is always determined by the ion which has the greater velocity of the two unlike ions, this always moving with the positive current. A few experiments were made with concentrated solutions, but the observed and calculated values do not agree. H. C.

Potential Difference of Dilute Solutions. By W. Nernst (*Ann. Phys. Chem.* [2], **45**, 360—369).—This paper consists for the most part of critical observations on the work of Negbaur (preceding abstract).

The author states that the osmotic pressure of dilute salt solutions, calculated by means of his theory from the electromotive activity of the ions, agrees within 1 or 2 per cent. with the osmotic pressure as derived from the theories of Van't Hoff and Arrhenius. The measurement of electromotive forces is thus, for dilute solutions at least, by far the most exact method of indirectly measuring osmotic pressure.

J. W.

Electromotive Activity of the Ions. By W. Nernst and R. Pauli (*Ann. Phys. Chem.* [2], **45**, 353—359).—The electromotive forces developed in liquid cells made by the combination of decinormal and centinormal solutions of potassium and hydrogen chlorides have been investigated experimentally by the authors, and the results obtained are compared with the numbers deduced from the osmotic pressure and dissociation hypothesis as developed in this direction by Nernst and Planck (compare Abstr., 1890, 1355). The agreement between observation and theory is satisfactory. As solutions of zinc sulphate and of copper sulphate having equal molecular concentrations are very nearly equally dissociated into ions, it follows from the theory that there should be no considerable E.M.F. at their surface of contact. By investigating the combination

$$Hg \mid HgSO_4 \mid 1/10n CuSO_4 \mid 1/10n ZnSO_4 \mid HgSO_4 \mid Hg,$$

the authors find that in reality the E.M.F. is only 0·00024 volt. The seat of the E.M.F. in a Daniell element is consequently not to be sought for at the contact of the two liquids. J. W.

Conductivity of Lead Dioxide. By J. Shields (*Chem. News*, **65**, 87).—Both the hydrated lead dioxide, PbO_2,H_2O, prepared by electrolysing a solution of sodium lead tartrate, and lead dioxide prepared by Wöhler's method, were examined by placing a layer of the oxide between two conducting surfaces connected with the terminals of a battery and watching for polarisation currents on breaking the circuit, and also by the method employed by Streintz. The results show that both forms of oxide conduct metallically and neither of them electrolytically. The specific resistances of these two preparations are:—

	C.G.S. units.
Chemically prepared dioxide.....	$5{\cdot}59 \times 10^9$
Electrolytically prepared dioxide....	$6{\cdot}78 \times 10^9$

D. A. L.

Magnetism and Atomic Weight. By P. Bachmetéeff (*Ber.*, **25**, 566—569).—In a previous paper (*J. Russ. Chem Soc.*, 1889, 39), the author discussed the relation between the magnetic properties of the elements and their atomic weights; his conclusions have, however, been disputed by Errara (Abstr., 1891, 518), who maintains that no relationship can be traced except in so far as the elements in Mendeléeff's odd series are diamagnetic and in the even series paramagnetic.

The author in reply points out that a considerable number of the elements do not obey Errara's rule, and that many of the elements now supposed to be paramagnetic are probably in reality diamagnetic, the observed paramagnetism being due to the presence of small quantities of iron; thus, natural platinum, which contains iron, is paramagnetic, whereas the pure metal is diamagnetic. There are at least eight exceptions to Errara's rule, and no single exception to that previously given by the author; the latter, therefore, believes his system to be the more trustworthy. H. G. C.

Magnetism of Organic Compounds. By S. Henrichsen (*Ann. Phys. Chem.* [2], **45**, 38—61).—The author has investigated the magnetic constants of a considerable number of organic compounds under varying conditions. All the substances studied behaved similarly with respect to the magnetising force: as the force K increased, the quotient A/K^2, where A is the diamagnetic deflection, rose slightly and then fell off. Propyl formate, for example, gave the following numbers:—

K.	A.	A/K^2.
82·7	32·3	0·00595
116·0	65·4	0·00612
146·1	103·6	0·00613
178·6	152·4	0·00602

The function A/K^2 is considered by the author to be in reality constant.

Measurements of the temperature coefficient, between 20° and 90°, gave values of a for the different substances ranging from 0·00103 to

0·00156 in the formula $M_t = M_o\ (1 + at)$, where M is the magnetism. $a = 0{\cdot}00133$ may be adopted as the mean for all the compounds investigated.

Several measurements in absolute units are given. J. W.

Specific Heat of Aluminium. By J. W. Richards (*Chem. News*, **65**, 97—98).—Inasmuch as the recorded numbers for the specific heat of aluminium differ widely, the author has redetermined it, at temperatures between 16° and 22°, by noting the reduction in temperature produced by 100 or 200 grams of aluminium in a known weight of water at a higher temperature; at temperatures between 20° and 100°, by dropping aluminium, from suspension in steam, into water in a calorimeter; and at temperatures from 120° to 600° by heating a ball of platinum and a ball of aluminium placed together on a platinum support in the same air-bath or furnace and dropping them simultaneously into two exactly similar calorimeters; the platinum results furnished the data for calculating the values for the aluminium. The latter method gave most concordant results; selecting the best experiments and correlating the data by the method of least squares, the following formulæ are obtained, 0·2220 being the true specific heat at 0°.

$$Sm = 0{\cdot}2220 + 0{\cdot}00005(t_1 + t_2),$$
$$S = 0{\cdot}2220 + 0{\cdot}0001t,$$

making the sp. heat

At 20°	0·2240	Total caloric capacity to the melting point	158·3.
„ 100	0·2320		
„ 625 (melting point)	0·2845		

This gives 6·13 as the atomic heat, using the mean specific heat between 0° and 100°. D. A. L.

Use of Compressed Oxygen in the Calorimetric Bomb. By Berthelot (*Compt. rend.*, **114**, 318—319).—If the oxygen that is used has been kept in a gas-holder over water, it is saturated with aqueous vapour, and when compressed in the bomb sufficient water is condensed to again saturate the gas at the end of the experiment. The difference in the tension of the aqueous vapour resulting from the difference between the initial and final temperatures (usually about 3°) would introduce an error of less than half a minor calorie, which is negligible in all ordinary cases. If, on the other hand, commercial compressed oxygen is used, the gas is practically dry. It follows that in most cases some of the water produced by the combination will evaporate in order to saturate the gas in the bomb. The absorption of heat from this cause will amount to from 2 to 3·5 cal. in a bomb of about 330 c.c. capacity, and to 5 or 6 cal. in a bomb of 600 to 700 c.c. capacity. C. H. B.

Reconversion of Heat into Chemical Energy by Production of Water Generator Gas and Carbonic Anhydride Generator Gas. By A. Naumann (*Ber.*, **25**, 556—562).—The production of water

gas from carbon and liquid water, $H_2O + C = H_2 + CO$, is an endothermic reaction, and involves an absorption of 38,770 cal. Generator gas produced from air and carbon is formed with evolution of heat, the reaction $C + O = CO$ giving rise to a development of 29,690 cal. The heat evolved in the latter reaction would serve to raise the temperature of the products formed through 2169°, and if then cooled to 15° before being used, the whole of the heat of formation would be lost and the heat of combustion, 67,960 cal., of the carbonic oxide alone remain. The loss here involved is 30·4 per cent. of the heat of combustion, 97,650 cal., of the original carbon.

In order to avoid the above loss, the formation of water gas may be combined with that of generator gas, as in the Dowson process, or, in place of water, carbonic anhydride may be mixed with the air passed over the heated carbon, the reaction $CO_2 + C = 2CO$ being endothermic and involving an absorption of 38,270 cal. The mixture of water or carbonic anhydride might be made in such proportion that neither absorption nor development of heat would take place. In this case the following table gives the calculated values of the heats of combustion of 1 litre of each gas in the first column; the increase in the temperature of the flame, calculated from the heats of combustion and specific heats of the mixed gases, in the second column; and the heat obtainable from the combustible gases present in 1 litre of each gas when cooled through 1°, in the third column.

Gas.	I.	II.	III.
	cal.		cal.
Generator gas	1044	1904°	0·5487
Carbonic anhydride generator gas	1739	2449	0·7101
Water generator gas, from liquid water at 15°.	1652	2356	0·7016
Water generator gas, from gaseous water at 15°	1790	2431	0·7363
Water gas	2812	2830	0·9934

The advantage of water generator gas or carbonic anhydride generator gas above ordinary generator gas is at once apparent.

H. C.

Thermochemistry of Sodium Isopropoxide. By de Forcrand (*Compt. rend.*, **114**, 420—422).—In dilute solutions (1 equivalent in 4 litres) sodium hydroxide and isopropyl alcohol are without action on one another, and it follows that at this degree of dilution sodium isopropoxide is completely dissociated.

Heat of dissolution of sodium isopropoxide at +12° = +16·40 Cal.; heat of dissolution of isopropyl alcohol +3·64. It follows that—

C_3H_8O liq. + Na sol. = H + C_3H_7NaO sol.	develops	+30·27 Cal.
C_3H_8O liq. + $\frac{1}{2}Na_2O$ sol. = $\frac{1}{2}H_2O$ sol. + C_3H_7NaO sol.	,,	+15·405 ,,
C_3H_8O liq. + NaOH sol. = H_2O sol. + C_3H_7NaO sol.	,,	−1·60 ,,
$C_3 + H_7 + Na$ (sol.) + O = C_3H_7NaO sol.	,,	+108·77 ,,

The corresponding values with primary propyl alcohol are:— +32·52, +17·66, +0·65, and +108·65 respectively.

The compounds of sodium glycol with isopropyl alcohol recently described (this vol., p. 691) gave the following results:—

Heat of dissolution, $C_3H_7NaO,3C_3H_8O$ = 14·47 Cal.
Heat of dissolution, $C_2H_5NaO,3C_3H_8O$ = 11·81 ,,
C_3H_7NaO + $3C_3H_8O$ develops +0·13 Cal.
C_2H_5NaO + $3C_3H_8O$,, −0·08 ,,

therefore—

C_3H_7NaO sol. + $3C_3H_8O$ liq. = $C_3H_7NaO,3C_3H_8O$ sol. ..... develops +12·98 Cal.
C_2H_5NaO sol. + $3C_3H_8O$ liq. = $C_2H_5NaO,3C_3H_8O$ sol. ..... ,, + 5·04 ,,
$4C_3H_8O$ liq. + Na sol. = H gas + $C_3H_7NaO,3C_3H_8O$ sol. ..... ,, +43·25 ,,

The last value is higher than the heat developed by the action of sodium on water. The dissolution of the compound

$$C_3H_7NaO,3C_3H_8O$$

in excess of isopropyl alcohol absorbs −2·63 Cal., and hence

$80C_3H_8O$ liq. + Na sol. = H gas + C_3H_7NaO diss. in $79C_3H_8O$ liq. ..... develops +40·62 Cal.

The action of sodium on isopropyl alcohol develops nearly 3 Cal. less than its action on normal propyl alcohol. Isopropyl alcohol differs from the other monhydric alcohols in that the dissolution of the solid $C_3H_7NaO,3C_3H_8O$ in excess of the alcohol is endothermic, whereas the heat of formation of the compound itself is exothermic, and amounts to +12·28 Cal. It would follow that the excess of alcohol simply dissolves the crystallisable compound without formation of polyalcoholic combinations. Similar phenomena are shown by barium hydroxide, and the hydrate $Ba(OH)_2,8H_2O$, and the corresponding strontium compounds. C. H. B.

Tartronic Acid and Alkaline Tartronates. By G. Massol (*Compt. rend.*, **114**, 422—424).—The tartronic acid used was in large, transparent, anhydrous prisms melting at 155°, with evolution of carbonic anhydride; heat of dissolution, −3·75 Cal.

$C_3H_4O_5$ + KOH. ..... develops +13·77 Cal.
$C_3H_3KO_5$ + KOH. ..... ,, +12·48 ,,
$C_3H_4O_5$ + 2KOH ..... ,, +26·25 ,,

The potassium hydrogen tartronate forms large, very oblique prisms with a rhombic base; these contain $\frac{1}{2}$ mol. H_2O, and become anhydrous at 110°; heat of dissolution of the anhydrous salt, −7·5 Cal. The normal tartronate forms large, anhydrous crystals; heat of dissolution, −4·75 Cal.

$C_3H_4O_5 + NaOH$	develops	+13·75 Cal.
$C_3H_3O_5Na + NaOH$	,,	+13·65 ,,
$C_3H_4O_5 + 2NaOH$	,,	+27·40 ,,

The normal salt forms a very deliquescent, crystalline mass, which becomes anhydrous at 110° without further decomposition; heat of dissolution, −3·00 Cal. The acid salt, when evaporated to dryness on a water-bath, becomes partially converted into glycollate.

$C_3H_4O_5$ sol. + KOH sol. = $C_3H_3O_5K$ sol. + H_2O sol.	develops	+31·4 Cal.
$C_3H_3O_5K$ sol. + KOH sol. = $C_3H_2O_5K_2$ sol. + H_2O sol.	,,	+23·6 ,,
$C_3H_4O_5$ sol. + 2KOH sol. = $C_3H_2O_5K_2$ sol. + $2H_2O$ sol.....	,,	+55·0 ,,
$C_3H_4O_5$ sol. + 2NaOH sol. = $C_3H_2O_5Na_2$ sol. + $2H_2O$ sol.....	,,	+49·07 ,,

The corresponding values for malonic acid are about 4 Cal. per equivalent lower, a result similar to that obtained with succinic and the hydroxysuccinic acids. C. H. B.

Heat of Dissolution of Salts in Water. By R. Scholz (*Ann. Phys. Chem.* [2], **45**, 193—206).—The author has determined the heat of dissolution of various salts in water at 0° by means of Bunsen's ice calorimeter. *N* in the following table (p. 677) denotes the number of gram-equivalents of salt dissolved in a litre of water; the numbers in the other columns are the small calories evolved per gram of salt dissolved:—

These results are not in harmony with those of Staub (*Inaug. Diss., Zurich*, 1890), who employed the same method. J. W.

Theory of Heat of Dissolution and of Osmotic Pressure. By C. Dieterici (*Ann. Phys. Chem.* [2], **45**, 207—237).—Van't Hoff deduced the laws regulating the vapour pressures of solutions from the laws of osmotic pressure. The author proceeds in the reverse way from the vapour pressure of dilute aqueous salt solutions, and arrives at the following conclusions:—

1. Raoult's laws for vapour pressure are capable of explanation by adopting views borrowed from the kinetic theory of gases.

2. It then follows from the principles of thermodynamics that, when two miscible liquids with different vapour pressures are capable of interdiffusion, there must be between them a diffusion pressure which can be calculated from the difference of vapour pressure if both liquids give off the same substance as vapour.

3. The hydrostatic pressure which is equal and oppositely directed to the diffusion pressure is Van't Hoff's osmotic pressure.

4. At great dilutions this is proportional to the relative lowering of the vapour pressure, but is not so in more concentrated solutions.

5. The rule that the osmotic pressure is proportional to the absolute temperature is only valid for the temperatures at which the laws

N.	NaCl.	KCl.	$NaNO_3$.	KNO_3.	$\frac{1}{2}(CuSO_4 + 5H_2O)$.	$\frac{1}{2}K_2SO_4$.	KI.	KBr.
0·0625	33·07	71·59	69·93	93·55	—	48·57	35·24	48·83
0·125	33 25	71·29	68·53	92·99	13·60	48·26	35·46	48·82
0 25	32·62	70·84	66·46	90·75	13·38	47·06	34·82	48·72
0·5	30·60	69·59	—	87·55	12·98	45·14	33·88	47·62
0·977	—	—	—	—	—	42·09	—	—
1·0	27·13	66 95	58·75	82·00	12·64	—	32·52	46·04
1·3	—	—	—	79·42	—	—	—	—
1·5	—	—	54·95	—	—	—	—	—
2·0	21·02	63·18	—	—	—	—	29·88	43 08
2·5	—	—	—	—	11·43	—	—	—
3·6	—	58·29	—	—	—	—	—	—
4·0	13·18	—	43·18	—	—	—	26·03	38·99
6·0	9·00	—	—	—	—	—	—	—
7·5	—	—	—	—	—	—	22·06	—
8·0	—	35·31	—	—	—	—	—	—

of Boyle and Charles hold good for the vapour of the solvent, and only then so far as von Babo's law is true.

6. Whilst these principles justify the analogy of gaseous substances with substances in solution, it does not follow that substances in solution are really in the gaseous state, or that the osmotic pressure is of kinetic origin.

7. When a salt is dissolved in a solvent a certain external work, the osmotic work, can be done. If the dissolution is effected, as is usual, by mixing the salt and the solvent, this work is not done, and thus the process is irreversible.

8. Molecular forces (of kinetic nature) between the salt and the solvent perform the osmotic work. J. W.

Freezing Point of Dilute Solutions of Cane Sugar. By RAOULT (*Compt. rend.*, **114**, 268—271, and *Zeit. physikal. Chem.*, **9**, 343).—The author has modified his apparatus for determining freezing points, with a view to secure more regular cooling, and he finds it possible to obtain results accurate to 0·002 of a degree. The following results were obtained with dilute solutions of cane sugar:—

Weight of sugar in 100 grams of water.	Reduction of freezing point.	Molecular reduction of freezing point.
0·683	0·042°	20·9
1·426	0·086	20·6
2·154	0·128	20·3
2·848	0·168	20·1
4·329	0·252	19·9
5·859	0·340	19·8
7·297	0·422	19·8
11·132	0·652	20·0
16·098	0·956	20·3
39·040	2·274	21·6

If the reductions of the freezing point are taken as abscissæ, and the molecular reductions as ordinates, the latter are represented by a curve which, except in the point of origin, coincides with that previously given (*Ann. Chim. Phys.* [6], **8**). The result confirms the author's previous statement, that with cane sugar, as with other substances, the molecular reduction increases below a certain degree of dilution. The increase is, however, so small, that it seems to confirm the views of Arrhenius (compare *Zeit. physikal. Chem.*, **2**, 561). C. H. B.

The Cryoscopic Behaviour of Weak Solutions. Part I. Sulphuric Acid. By S. U. PICKERING (*Ber.*, **25**, 1099—1107).—The author gives a critical examination of his previous results (Trans., 1890, 342), using an improved method of plotting out the results, and describing a new method of estimating the experimental error, and also the error of a drawing made to represent a series of results. He finds that his original representation of his results with sulphuric acid, according to which three changes of curvature existed, attributes a mean apparent error to the points exactly equal to the ascertained

mean experimental error, 0·0008°, whereas no drawing can be made with a lath so as to obliterate any of these "breaks" without increasing the apparent error to an unwarrantable extent. A drawing obliterating all the breaks shows an error 6·3 times greater than the experimental error. The values calculated according to Van't Hoff's formula and the dissociation hypothesis do not agree within experimental error with the observed values; the total error up to a depression of 0·7° is 870 greater than it should be, and even imagining the existence of some regular but unknown source of error, this value cannot be reduced to less than 16. The best agreement extends only to 0·4°, and even here it is, with every favourable allowance, not within the experimental error, being 6—9 times greater than this error.

S. U. P.

Apparatus for the indirect Determination of Vapour Pressures. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **10**, 132—134; compare Abstr., 1891, 781).—This consists essentially of an inverted V-tube, to the angle of which a narrow tube furnished with an air-tight stopcock is fused, and to the free ends of the Λ-tube two small, 30—40 c.c., flasks are accurately adapted. The salt whose hygroscopicity is to be determined is placed in one flask, and sulphuric acid of known strength in the other, and a vacuum is induced in the apparatus, which is maintained for 3—4 weeks at a constant temperature. The sulphuric acid is then titrated, and the vapour pressure calculated by aid of Regnault's tables (compare also Müller-Erzbach, Abstr., 1889, 1045).

T. G. N.

Stereochemical Models of Organic Molecules. By A. Eiloart (*Amer. Chem. J.*, **13**, 559—564).—Carbon atoms are represented by tetrahedra, which may be connected either corner to corner to represent the ethane condition, or edge to edge to represent the ethylene condition; and the elements and radicles attached to the carbon atoms are represented by caps, on which their symbols and formulæ are inscribed, which fit over the corner of the tetrahedra. In this way the modern views as to the constitution of such compounds as the lactic acids, the tartaric acids, maleïc and fumaric acids, and the hydrophthalic acids may be made clear. Full details of construction, as well as numerous examples, are given.

Jn. W.

Lecture Experiment: Burning Sulphur in Oxygen. By W. A. Noyes (*Amer. Chem. J.*, **13**, 553).—A 250 c.c. flask containing a fragment of sulphur, and filled with oxygen by downward displacement, is fitted in a horizontal position to one end of the transverse and horizontal limb of a T-piece, the other end of which communicates through a stopcock with a filter-pump, whilst the vertical limb dips into mercury and serves as a pressure gauge.

The pressure in the flask having been reduced to about 450 mm., the stopcock is turned off, and the level of the mercury in the gauge marked by a strip of paper. The sulphur is then ignited by heating the flask with a small flame, and is seen to burn quietly in the rarefied oxygen. When the combustion is finished, the flask quickly cools to the original temperature, and the mercury is seen to return

to its original level, thus showing that the volume of the sulphurous anhydride is the same as that of the oxygen from which it has been formed. Jn. W.

Inorganic Chemistry.

Boiling Point of Zinc Chloride and Bromide, and Ignition Temperature of Electrolytic Gas. By F. Freyer and V. Meyer (*Ber.*, **25**, 622—635).—In a previous paper (Abstr., 1891, 1153), Krause and Meyer have shown that electrolytic gas, when slowly passing through a glass tube, does not explode at 606° (the boiling point of stannous chloride). In order to get a nearer approximation to the point of ignition of the gas, the authors have passed the gas through a tube contained in a bath of boiling zinc chloride and zinc bromide, the boiling points of which they find to be 730° and 650° respectively. With the former, explosion takes place whether the gas is wet or dry, but in the boiling bromide no appreciable combination takes place, and the temperature of ignition therefore lies between these two points.

The bath employed in the experiments consisted of a sheet-iron crucible 10 cm. in height and 6 cm. in diameter, to the lid of which was brazed a sheet-iron tube 2 cm. in diameter, and reaching to within about a short distance of the bottom of the crucible. The tube conveying the electrolytic gas is widened out at one point into a long bulb, which is wholly immersed in the inner sheet-iron tube. To ascertain the boiling point of the chloride and bromide, an air thermometer made of platinum was inserted in the iron tube, no glass being found which could withstand the temperature without partially collapsing.

The explosion in the zinc chloride only takes place with certainty if the gas is passed through the tube when the zinc chloride is already at the boiling point, and is then sufficiently violent to pass along tubes only $\frac{1}{3}$ mm. in diameter. If the gas be passed through the tube whilst the zinc chloride is being heated, the gases slowly combine, forming water without explosion. H. G. C.

Action of Nascent Hydrogen and Nascent Oxygen on Nitric Acid. By W. F. Hall (*Amer. Chem. J.*, **13**, 564—570).—A steady electrical current, averaging about 11 coulombs per day, was passed through dilute, aqueous nitric acid (sp. gr. 1·069 at 20°) for 84 days. The electrodes were arranged in separate vessels, connected by a siphon filled with the electrolyte, and the evolved gases were collected separately.

The rate of evolution of hydrogen at the cathode gradually diminished, and on the 59th day vanished; but it could always be temporarily and largely augmented by agitation. The specific gravity of the electrolyte steadily diminished (finally to 1·034 at 27°), owing to

reduction of the nitric acid to ammonium nitrate, the formation of which took place slowly at first, but afterwards with increasing rapidity.

The rate of evolution of oxygen at the anode was at first much greater in proportion than that of the hydrogen at the cathode, but it decreased after a few days to the normal amount, and continued to decrease until the end of the experiment. As in the previous case, the flow could at any time be temporarily and largely augmented by agitation. The specific gravity of the electrolyte steadily increased (finally to 1·079 at 27°), owing, probably, to the conversion of the nitric acid into orthonitric acid, H_3NO_4. Jn. W.

Decomposition of Sulphurous Anhydride by Carbon at High Temperatures. By Scheurer-Kestner (*Compt. rend.*, **114**, 296—298).—When sulphurous anhydride is passed over carbon heated to bright redness, it is decomposed in accordance with the equation $2SO_2 + 3C = 2CO + CO_2 + S_2$. It is possible that carbon bisulphide and carbon oxysulphide are formed as intermediate products.

The result confirms the author's view as to the nature of the reaction between a sulphate, silica, and carbon at a high temperature. The sulphate is converted into a silicate and sulphuric anhydride; the latter is decomposed by heat into oxygen and sulphurous anhydride, and these in presence of carbon yield carbonic anhydride, carbonic oxide, and oxygen, $3RSO_4 + 6SiO_2 + 5C = 3(RO,2SiO_2) + 3S + 4CO_2 + CO$. C. H. B.

Action of Iodine on Sodium Hydrogen Sulphite. By W. Spring and E. Bourgeois (*Arch. Pharm.*, **229**, 707—710).—Referring to the results obtained by Otto and Holst (Abstr., 1891, 978), the authors point out that their previous work on this subject showed that there was no formation of dithionic acid (Abstr., 1886, 978). In order to test the accuracy of Otto's results, each of the authors repeated his work independently of the other in different laboratories, but could detect no dithionic acid. They further determined the amounts of iodine used during the oxidation, and these in every case corresponded with the equation

$$2NaHSO_3 + 2I_2 + 2H_2O = 2NaHSO_4 + 4HI,$$

whilst only half this amount of iodine is required for the formation of dithionic acid. J. W. L.

Amorphous Boron. By H. Moissan (*Compt. rend.*, **114**, 319—324).—The author has prepared amorphous boron by the various known methods, and has analysed the products; the results are contained in the following table (p. 682):—

No. 1 was prepared by the method of Gay-Lussac and Thenard, using a copper tube. Hydrochloric acid removes part of the potassium, but, even after repeated washing with this acid and water, the residue contains about 7 per cent. of potassium. No. 2 was obtained by the action of sodium on boric anhydride in presence of sodium chloride, the product being washed with hydrochloric acid and dried

	1.	2.	3.	4.	5.
Boron	44·1	62·50	71·97	32·38	51·15
Boric acid (H_3BO_3)	17·8	15·65	13·50	42·52	23·07
Potassium	14·4	—	—	—	6·00
Copper	12·5	—	—	—	—
Iron	5·8	4·61	5·04	7·51	3·06
Sodium	—	6·63	3·89	10·34	—
Boron nitride	—	5·84	5·28	2·26	8·75
Hydrogen	—	0·44	?	} 4·10 {	—
Water	—	—	—		—
Insoluble matter	4·9	—	—	—	—
Not estimated	—	4·33	—	—	—
	99·5	100·00	99·68	99·11	92·03

in a vacuum or in an atmosphere of hydrogen. No. 3 is the same product after prolonged treatment with boiling hydrochloric acid, and No. 4 a similar product after prolonged treatment with water. No. 5 was obtained by Berzelius' method, namely, the action of potassium on excess of potassium borofluoride.

The product (No. 2), obtained by the method of Deville and Wöhler, contains a small quantity of boron hydride, gives off hydrogen at 250—275°, and yields hydrogen phosphide when heated in phosphorus trifluoride.

Iron boride is obtained as a grey mass by the action of boron chloride on iron reduced by hydrogen. C. H. B.

Preparation of Amorphous Boron. By H. Moissan (*Compt. rend.*, **114**, 392—397).—When a current of 35 ampères is passed through boric anhydride mixed with 20 per cent. of sodium borate and heated at 1200°, boron is liberated, but immediately recombines with oxygen with vivid incandescence.

It is well known that when boric anhydride is heated with the theoretical quantity or an excess of magnesium, reduction takes place with formation of magnesium borides. The author finds that if the boric anhydride is in considerable excess different results are obtained. There are two magnesium borides, one unstable and decomposed by water with liberation of hydrogen and boron hydride, the other stable and not affected by water, hydrochloric acid, or nitric acid.

70 grams of finely-powdered magnesium free from iron and silicon, was intimately mixed with 210 grams of recently fused boric anhydride. The mixture was heated to bright redness in a clay crucible, and in a few minutes an energetic reaction took place. The central part of the product was boiled with water and hydrochloric acid until the magnesium borate was removed, then treated for a long time with successive quantities of pure boiling hydrochloric acid, washed with water, treated with alcoholic potash, again washed with water, boiled for several hours with hydrofluoric acid, washed with water, and dried in a vacuum. The product is a very light maroon powder which does not alter when exposed to air; it contains 94 to

95 per cent. of boron, 2·3 to 3·75 per cent. of magnesium, and 1·2 to 1·6 per cent. of insoluble matter.

If this product is fused with 50 times its weight of boric anhydride, and the product treated in the same way as the original product, a maroon powder is obtained containing only traces of magnesium.

One product contained boron, 98·30; magnesium, 0·37; insoluble, 1·18 = 99·85.

If the boron is required perfectly free from nitride, reduction must be effected in a crucible brasqued with a mixture of finely powdered titanic oxide and carbon; the product contains from 92·6 to 99·2 per cent. of boron. Boric anhydride may also be reduced by magnesium in porcelain dishes in an atmosphere of hydrogen, and a very pure product is obtained, but the yield is small. C. H. B.

Explosion of Ammonium Nitrate. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **10**, 127—134).—Ammonium nitrate is a component of many explosives which are but slightly sensitive to ordinary mechanical shocks, and are difficult of ignition, although by the detonation of small quantities of mercuric fulminate they are rendered explosive. Berthelot (Abstr., 1882, 453) and Thorpe (Trans., 1889, 220) prove that endothermic combinations decompose explosively under the influence of mercuric fulminate, and it is well known that explosives require a variable initial impulse to cause their decomposition. The author describes the following experiments which were made with shells of 8 cm. calibre, weighing 7 kilos., and capable of holding about 200 grams of explosive. The force of the explosion was estimated by the number and weight of the collected pieces and the distance to which they were scattered, the difference between this weight and the original weight being reckoned as shell reduced to powder by the explosion. In the case of black gunpowder fired electrically by a platinum thread, 10 pieces were collected whose collective weight was nearly that of the original shell, but, when a fulminate cap was used, 77 pieces whose collective weight was but 3·8 kilos. were obtained. When shells filled with bellite, dynamite, and cotton-powder were exploded by means of 1 gram of mercuric fulminate, the shells were reduced to powder. 1 gram of mercuric fulminate produced no effect on a shell filled with ammonium nitrate except to evaporate a small amount in the immediate vicinity of the fuze, whilst the screw holding the shell was moved. 3 grams of fulminate caused a low, rumbling explosion, and 62 pieces of shell were collected which weighed 6 kilos. A shell containing 180 grams of ammonium nitrate and 20—30 grams of bellite (composed of dinitrobenzene 1 part and ammonium nitrate 4 parts) yielded, on explosion by 1 gram of mercuric fulminate, 230 pieces weighing 2·75 kilos. Hence it appears that ammonium nitrate requires a stronger initial impulse than either dynamite or dry cotton-powder; that its employment, unless it be mixed with charcoal or aromatic nitro-compounds, is negatived on account of its weaker action, although for coal mining purposes its employment would seem to be advantageous, as but a slight rise in temperature accompanies the explosion. T. G. N.

Silver Sulphite. By W. H. Sodeau (*Chem. News*, **65**, 102).—Silver sulphite was prepared by passing sulphurous anhydride into a solution of recrystallised silver nitrate, washing well, and drying in a vacuum over sulphuric and chromic acids mixed; when sealed up in tubes, it was blackened slowly and slightly by a fortnight's exposure to ordinary sunlight, and, in other experiments, more intensely and more readily as the temperature, at which it was exposed, was raised. The presence of water also accelerates the blackening. D. A. L.

Silver Nitrosilicate: Existence of a Nitrosilicic Acid. By G. Rousseau and G. Tite (*Compt. rend.*, **114**, 294—296).—When silver nitrate is heated with a small quantity of water and fragments of marble in sealed tubes at 180—300° for many hours, deep ruby crystals are obtained, adhering strongly to the sides of the tube. They have the composition $2AgNO_3,3Ag_4SiO_4$ or

$$7Ag_2O,3SiO_2,N_2O_5.$$

Similar results are obtained if finely-divided silica is added to the contents of the tube, and in this case the crystals do not adhere to the glass. Silver oxide may be used in place of calcium carbonate, but the excess is difficult to separate at the end of the operation. The same product is obtained in smaller crystals by heating silver nitrate with silica at 350—440°.

Silver nitrosilicate forms short, ruby prisms showing longitudinal extinction in parallel light. When heated to dull redness, the crystals intumesce with evolution of nitrogen oxides, and a residue of metallic silver and the silicate Ag_2SiO_3 is left. The nitrosilicate is easily soluble in dilute nitric acid, but after some time, and especially on heating, silica separates. Hydrochloric acid decomposes the compound immediately with separation of silver chloride. Ammonium chloride also decomposes it, and the solution smells of ammonia, but nitrosilicic acid could not be isolated. Potassium chloride solution is without action even at 100°, but potassium iodide yields silver iodide and potassium nitrosilicate, the latter separating in long needles when the filtrate from the silver iodide is concentrated in a vacuum.

C. H. B.

Solubility of Tricalcium Phosphate and Dicalcium Phosphate in Solutions of Phosphoric Acid. By H. Causse (*Compt. rend.*, **114**, 414—417).—The author has measured the solubility of tricalcium phosphate and dicalcium phosphate respectively in 100 c.c. of solutions containing 5, 10, 15, 20, 25, 30 grams of phosphoric acid respectively. With more than 30 grams of phosphoric acid, monocalcium phosphate is precipitated.

	1.	2.	3.	4.	5.	6.
Tricalcium phosphate dissolved.....	3·85	7·28	9·45	12·50	13·79	15·10
Dicalcium phosphate dissolved.....	4·30	7·15	9·30	11·86	13·40	15·10

With tricalcium phosphate, when the solutions are heated at 100°,

there is a precipitate of dicalcium phosphate in Nos. 5 and 6; with dicalcium phosphate, under similar conditions, there is a precipitate in all six solutions.

It will be observed that the solubility of tricalcium phosphate is greater than that of dicalcium phosphate. A condition of equilibrium seems to be established between phosphoric acid, monocalcium phosphate, and water, the water playing the principal part and determining the proportion of free phosphoric acid and monocalcium phosphate. C. H. B.

Barium Carbide. By Maquenne (*Compt. rend.*, **114**, 361—362).—When barium amalgam is mixed with powdered charcoal and distilled in a current of pure and dry hydrogen, a somewhat energetic reaction takes place at a red heat without any absorption of gas. The product is a grey, fritted mass containing excess of carbon. It does not change at a bright red heat, but is immediately decomposed by cold water with evolution of acetylene mixed with 7 per cent. of some gas not absorbed by cuprous chloride. The formula of the carbide is BaC_2. It contains no hydrogen and its formation takes place readily in an atmosphere of nitrogen. In this case, however, barium cyanide is formed in quantity equal to about 25 per cent. of the original weight of the barium. The decomposition of the carbide by water is represented by the equation $BaC_2 + 2H_2O = C_2H_2 + Ba(OH)_2$.

If the property of forming carbides is common to other metals, this fact may throw some light on the natural formation of hydrocarbons, since Berthelot has shown that acetylene is the starting point in the synthesis of these compounds. C. H. B.

Lead Chlorosulphide and Bromosulphide. By F. Parmentier (*Compt. rend.*, **114**, 298—301).—Lead chloride is dissolved in hydrochloric acid, the solution diluted with water, and hydrogen sulphide is allowed to play on the surface of the liquid until yellow striæ become visible. The liquid is then rapidly agitated and poured into a large, dry vessel. A cinnabar-coloured precipitate of the chlorosulphide, $PbS,PbCl_2$, separates; it is very unstable, and is decomposed by water, acids, and alkalis. Alkalis at first blacken it, but the black substance rapidly changes to a white, flocculent mass. A similar change takes place, although slowly, when freshly precipitated lead sulphide is treated with an alkaline hydroxide.

Lead bromosulphide, $PbS,PbBr_2$, is obtained in a similar manner, but more readily; it is orange-yellow, and is unstable.

An iodosulphide also seems to exist, but its preparation is difficult on account of the slight solubility of lead iodide in hydriodic acid.

C. H. B.

So-called Mercurosammonium Compounds. By L. Pesci (*Gazzetta*, **21**, ii, 569—580; compare Abstr., 1891, 268).—The author has examined most of the so-called mercurosammonium compounds, obtained by treating mercurous salts with ammonia, and finds that they consist of the corresponding mercurammonium salts mixed with metallic mercury. The mercurammonium salts being readily soluble

in a saturated solution of ammonium sulphate containing ammonia, the metallic mercury can be separated from the precipitate.

When calomel is treated with ammonia, a grey powder ordinarily known as mercurosammonium chloride, NH_2Hg_2Cl, is obtained; this, on microscopical examination, is seen to contain metallic mercury, and on treating it with ammoniacal ammonium sulphate solution, it partially dissolves, leaving a residue of mercury. Under the action of light the product rapidly changes, but when preserved from such disturbing influences, the reaction between calomel and ammonia is probably represented by the equation

$$2Hg_2Cl_2 + 4NH_3 = Hg_2NCl,NH_4Cl + 2Hg + 2NH_4Cl.$$

This is confirmed by treating the precipitate with aqueous potash until the evolution of ammonia is at an end. The mercurammonium salt is thus converted into hydrated mercurammonium chloride, Hg_2NCl,H_2O; the mixture of this salt and mercury thus obtained gives satisfactory numbers on analysis.

In a similar manner, the reaction between mercurous sulphate and ammonia, supposed to yield a compound having the composition $(NH_2Hg_4O)_2SO_4$, is shown to proceed as represented by the equation $28Hg_2SO_4 + 56NH_3 + 12H_2O = 7(Hg_2N)_2SO_4,(NH_4)_2SO_4,12H_2O + 28Hg + 20(NH_4)_2SO_4$. The double salt loses ammonia when treated with aqueous alkalis, and gives hydrated mercurammonium sulphate, $(Hg_2N)_2SO_4,2H_2O$.

When a mercurous nitrate solution is allowed to remain in a slightly ammoniacal atmosphere, basic mercurous nitrate, $Hg_{10}N_6O_{20},2H_2O$, separates.

On treating mercurous nitrate solution with aqueous ammonia, a precipitate of variable composition is obtained. This reaction has given rise to considerable discussion owing to the therapeutic value formerly attributed to the product. The author shows that the reaction may be represented by the following equation:—$6Hg_2(NO_3)_2 + 12NH_3 + 2H_2O = 3Hg_2N\cdot NO_3,NH_4\cdot NO_3,2H_2O + 6Hg + 8NH_4\cdot NO_3$.

W. J. P.

Metals of the Cerium Group. By P. Schottländer (*Ber.*, **25**, 378—394).—The author gives details respecting the separation of the metals of the cerium group by Auer v. Welsbach's methods (*Monatsh.*, **5**, 508) under the following headings:—(I.) *Preparation of cerium salts free from lanthanum and didymium.* (II.) *Preparation of lanthanum and didymium salts free from cerium.* (III.) *Separation of lanthanum and didymium by the oxide process.* (IV.) *Preparation of pure lanthanum salts and partial separation of didymium into its constituents by crystallisation of ammonium didymium nitrate* (see *Wien. Acad. Ber.*, 1885, **2**, 317).

A. R. L.

Metals of the Cerium Group. By P. Schottländer (*Ber.*, **25**, 569—599).—This paper contains an account of the spectroscopic investigation of the didymium material described in the author's previous communication. The results obtained have not led to any very positive conclusions; they show, however, that every absorption maximum is not necessarily a characteristic of one distinct element,

as has been assumed by Krüss and Nilson (Abstr., 1887, 890), and that therefore the number of elements present in the material examined by the latter investigators is probably considerably less than they were led to conclude. H. G. C.

Action of Certain Liquids on Aluminium. By G. Lunge (*Chem. News*, 65, 110—111).—Adverse opinions having been expressed in connection with the application of aluminium to domestic, food storage, surgical and such like purposes, the author instituted the following experiments with commercial rolled sheet aluminium 1 mm. thick and containing per cent. 99·20 of aluminium, 0·55 of silicon, 0·25 of iron, and trace of copper. Suitable strips were cut from this, and after the edges and compressed rolled surface had been removed by filing, the strips were thoroughly cleaned by washing with soda, then successively with water, sulphuric acid, and again water, finally scrubbing with distilled water, rinsing with alcohol, and drying in an oven. Three strips were weighed and then suspended, without touching one another, from glass hooks, in corked flasks, containing about 400 c.c. of the liquids examined, comprising:—Ordinary claret and hock, brandy, pure 50 per cent. alcohol, solutions of tartaric, acetic, citric, lactic, butyric, boric, and salicylic acids, phenol, and tea, coffee, and beer. After six days, the strips were removed, washed, and weighed, and the experiments repeated for another period of six days. The results are tabulated in the paper, but the conclusions are that tea, coffee, and beer are practically without action on aluminium, brandy nearly so, whilst the action of acids and acid liquids, although more pronounced, is far too slight to cause any alarm; in the worst case, acetic acid, only 5 milligrams were dissolved per 100 c.c. in six days; and such action in a quart canteen, supposing it always to be full, would only amount to 1 gram in 200 days. The author hence asserts that aluminium may be employed without fear for holding articles of food, at least at the ordinary temperature.

D. A. L.

The Hypothetical Manganese Tetrachloride. By S. U. Pickering (*Phil. Mag.* [5], 33, 284).—If, when manganese dioxide is dissolved in hydrochloric acid, the sesquichloride is formed, some chlorine must be liberated at the same time; whereas, if the tetrachloride is formed, no chlorine need be liberated. Vernon's results (Abstr., 1892, 19), which tended to prove that the dissolution might be effected without evolution of chlorine, are, in the author's opinion, open to question. If the tetrachloride is formed, it would be possible to reproduce the whole of the dioxide taken by decomposing it with water; whereas, if it were the sesquichloride which were formed, only 50 per cent. of the dioxide taken could be thus recovered; yet, in spite of Vernon's experiments, which were supposed to show that the tetrachloride could be obtained almost undecomposed, he only in one case recovered a fraction more than the 50 per cent. of the dioxide, and he gives no analytical data to show what reliance can be placed on this excess (1·2 per cent.). In every other respect Vernon confirmed Pickering's conclusions (Trans., 1879, 654), and, in his (Pickering's) opinion,

adduces no evidence to disprove that the higher chloride is Mn_2Cl_5, or to prove that it is $MnCl_4$. S. U. P.

Bismuthic Acid. By G. André (*Compt. rend.*, **114**, 359—360).—Bismuthic acid combines very slowly and incompletely with potassium hydroxide, even when the latter is in excess. Prolonged boiling of the acid with an aqueous solution of ten times the quantity of potash required to saturate it yields a compound $KBiO_3,4HBiO_3$.

If, in the preparation of bismuthic acid, by the action of chlorine on bismuth oxide suspended in hot aqueous potash, the passage of chlorine is continued until the potash is completely saturated, a violet-black product is obtained that will not emulsify even after prolonged boiling with water. The product contains only a very small proportion of potassium, and sometimes it contains chlorine. After prolonged treatment with nitric acid and drying at 100°, it has the composition $Bi_2O_5,2HBiO_3$.

The emulsion obtained in the preparation of bismuthic acid (compare this vol., p. 413) is precipitated by dilute nitric acid, and the brown precipitate, when washed and dried at 100°, has the composition Bi_2O_5, or more probably $HBiO_3,Bi_2O_5$. C. H. B.

Note.—The author makes no reference to Mr. Pattison Muir's researches on this subject.–[Editors.]

Ruthenium Chloride and Hydroxychloride. By A. Joly (*Compt. rend.*, **114**, 291—293).—Chlorine attacks finely-divided ruthenium very slowly at 360° and converts it partially into the trichloride. If, however, the finely-divided metal is heated at 360° or 440° in a mixture of chlorine and carbonic oxide, care being taken that the chlorine is in excess, ruthenium trichloride is formed rapidly, and occupies many times the volume of the original metal. A small quantity of metal always remains unattacked. The chloride is a dark-brown substance, insoluble in cold water, inorganic and organic acids, carbon tetrachloride, carbon bisulphide, chloroform, phosphorus trichloride, or ether. When digested with 50 times its weight of absolute alcohol in sealed tubes for several hours, the chloride is dissolved, and the unattacked metal remains undissolved. Hot water slowly decomposes the chloride.

The solution of the chloride in absolute alcohol is purple-violet, but in presence of atmospheric moisture or if the alcohol is not quite anhydrous, the solution very slowly becomes violet-blue and afterwards deep indigo-blue. The change takes place more rapidly at 60°, and is due to the formation of a hydroxychloride, $RuCl_2{\cdot}OH$, which is obtained as a black product when the alcohol is distilled off, and is stable at 150°. It is very soluble in water, forming a deep indigo-blue solution, which gradually deposits ruthenium hydroxide, $Ru(OH)_3$.

If the hydroxychloride is dissolved in a considerable excess of hydrochloric acid, it forms a brown solution of a hydrochloride of the chloride, which is stable at about 150°, but at 200° is converted into the anhydrous chloride.

The hydroxychloride combines with ammonium and forms a compound very soluble in water; it yields an intense crimson solution, turning to yellow in presence of hydrochloric acid.

When ruthenium is subjected to the action of chlorine and carbonic oxide at 360° or 440°, a small quantity of a product containing carbonic oxide is formed. C. H. B.

Mineralogical Chemistry.

Elaterite and Dopplerite. By W. Alexéeff (*Zeit. Kryst. Min.*, **20**, 187—188; from *Mining J., St. Petersburg*, **1**, 361—375).—The author has made an examination of the elaterites and dopplerites of the Caucasus. The so-called elaterite of the government of Kutais proves, on analysis, to be dopplerite, the analytical results being as follows:—

C.	H.	O + N.	Ash.	Total.
51·17	4·60	34·57	9·66	100·00

The percentage of hygroscopic water was 7·28.

In composition, this mineral is very similar to the coal of Lepsia, in the Northern Ural. The author regards dopplerite as intermediate between bituminous coal and lignite. Pure elaterites are probably nothing more than asphalt, $n(CH_2)$, with which a small proportion of an oxygen compound is mixed. Elaterite from Sakupris Gelle, in the government of Kutais, gave, on analysis:—

C.	H.	O + N.	Ash.	Total.
84·66	8·19	4·98	2·19	100·02

B. H. B.

Manganese Hydroxide from the Euganeen, Italy. By G. di Boccard (*Zeit. Kryst. Min.*, **20**, 175—176; from *Riv. min. crist. ital.*, **4**, 55).—A black substance, consisting of manganese hydroxide, limonite, and sand, was found coating trachyte and calcite in geodes in the trachyte. It had a sp. gr. of 3·13 and a hardness of 5. Neglecting the sand, the analysis gave:—

Mn_2O_3.	Fe_2O_3.	H_2O.
75·51	6·80	17·69

An analysis of a similar substance, containing a larger proportion of limonite, yielded:—

Mn_2O_3.	Fe_2O_3.	H_2O.	Sand.
9·31	7·85	10·21	72·63

B. H. B.

Iron Ores of Central Russia. By P. A. Zemjatschensky (*Zeit. Kryst. Min.*, **20**, 184—186; from *Memoirs of the Soc. of Naturalists of St. Petersburg*, **20**, 1—300).—The author gives an exhaustive geological and chemical description of the iron ores of a portion of the Moscow coalfield. The ores are mostly brown hæmatites.

Numerous analyses are given, one of which, that of the ore from Katnoff, does not represent the composition of brown hæmatite but that of Hermann's turjite, its formula being $2Fe_2O_3,H_2O$. In physical properties, this mineral is similar to the turjite from the Turjin mine, in the Ural. In the ores of Dankoff, in some very compact brown hæmitites, crystals of a ferric hydrate occur, to which the author assigns the name of *hydrogoethite*. Its chemical formula is $3Fe_2O_3,4H_2O$, and its sp. gr. 3·556. The same mineral is also found in the ores occurring in the vicinity of Lipezk. B. H. B.

Vivianite. By W. Tjelouchin (*Zeit. Kryst. Min.*, **20**, 183; from *J. Russ. Chem. Soc.*, **21**, 129).—This mineral was found at Tamanj, on the Sea of Azov. The crystals, which occur in a fossiliferous rock, gave, on analysis, the following results:—

H_2O.	FeO.	Fe_2O_3.	P_2O_5.	CO_2.	CaO.	MgO.	Total.
29·41	37·05	3·07	28·23	0·15	0·54	2·01	100·46

B. H. B.

Natrolite from Monte Baldo. By G. Luzzatto (*Zeit. Kryst. Min.*, **20**, 175; from *Riv. min. crist. ital.*, **4**, 54).—An analysis of this mineral gave the following results:—

H_2O.	SiO_2.	Al_2O_3.	CaO.	Na_2O.	Total.
9·57	47·16	26·76	0·28	16·18	99·95

B. H. B.

Zoisite from Orenburg. By M. P. Melnikoff (*Zeit. Kryst. Min.*, **20**, 186; from *Material for Russian Geology*, **13**, 249—375).—This mineral occurs in the granite at Kulachta in fairly large crystals, and gave, on analysis, the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Loss on ignition.	Total.
40·48	31·71	2·07	23·50	2·51	100·27

B. H. B.

Organic Chemistry.

Fulminuric Acid. By P. Seidel (*Ber.*, **25**, 431—432).—*Ethyl fulminurate*, $C_3H_2N_3O_2{\cdot}OEt$, is obtained when silver fulminurate is heated with ethyl iodide at about 80—90° in a closed vessel; the yield is quantitative. It separates from a mixture of chloroform and acetone in crystals, melts at 133°, and decomposes at a slightly higher temperature; it is only very sparingly soluble in ether, ethyl iodide, light petroleum, benzene, cold water, and alcohol, but moderately easily in hot water and hot alcohol, and very readily in acetone. It dissolves unchanged in concentrated mineral acids, but is reprecipitated on the addition of water. When boiled for a long time with water and alcohol, it is decomposed with formation

of aldehyde and a crystalline acid; the last-named compound separates from water in large, colourless, efflorescent needles containing 1 mol. H_2O, and is very readily soluble in water, acetone, and alcohol; the anhydrous acid melts at 184°. F. S. K.

Decylene and its Derivatives. By L. Grosjean (*Ber.*, **25**, 478—481).—When castor oil is subjected to dry distillation under diminished pressure, a mixture of œnanthaldehyde and undecylenic acid, $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}COOH$, is obtained, and from the latter compound decylene is conveniently prepared by heating the barium salt (2 parts) dried at 120° with sodium ethoxide (1 part) in a retort, under a pressure of 50 mm. Decylene is a limpid, colourless liquid, insoluble in water; it boils at 61·5° under 15 mm. pressure, at 87—88° under 50 mm., at 106—107° under 100 mm., and at 172° under 760 mm., without decomposition. The sp. gr. at 0° = 0·7630, at 15° = 0·7512, and at 30° = 0·7398. The *dibromide* boils at 135° under 9 mm., and at 145° under 15 mm. pressure. The sp. gr. at 0° = 1·3841, at 15° = 1·3677, and at 30° = 1·3512. The *diacetate* was only obtained in an impure state as a colourless oil which boiled at 142° under 9 mm., at 152° under 14 mm., and at 264—272° at the ordinary pressure, with partial decomposition.

Decylene glycol is obtained by heating the diacetate with alcoholic potash in a reflux apparatus. It is a colourless, viscid liquid, boils at 145° under 15 mm., and at 255° under the ordinary pressure, without decomposition. The sp. gr. at 0° = 0·9226, at 15° = 0·9115, and at 30° = 0·9011.

Chlorodecyl benzoate, $C_{10}H_{20}Cl{\cdot}OBz$, is obtained by heating the above glycol (1 part) with benzoic chloride (0·807 part) for five hours at 120°, and then for one hour at 160°, and distilling the product under diminished pressure. It is a colourless oil, and boils at 201° under 12 mm.

Bromodecyl acetate, $C_{10}H_{20}Br{\cdot}OAc$, is obtained mixed with a small quantity of decylene dibromide by the action of silver acetate (1 mol.) on decylene dibromide. It boils at 146—147° under 15 mm. pressure, is a colourless oil, and, when boiled with alcoholic potash, is converted into a mixture of decylene glycol and decylene oxide, $C_{10}H_{20}O$. The latter boils at 85—86° under 10—11 mm. pressure, is very limpid, and has a penetrating odour. E. C. R.

Sodium Isopropoxide. By De Forcrand (*Compt. rend.*, **114**, 301—303).—When isopropyl alcohol is dehydrated by baryta and then twice distilled over sodium, the proportion of water is reduced to 0·5 per cent., and it boils at 82·2—82·8° (corr.); sp. gr. at 15° = 0·789.

When sodium is dissolved with the aid of heat in at least five equivalents of the alcohol, and the solution is allowed to cool, acicular crystals separate, which have the composition $C_3H_7NaO,3C_3H_8O$. If a solution of this compound is heated for some time with glycol, the compound $C_2H_5NaO_2,3C_3H_8O$ is obtained, and it also forms acicular crystals. Attempts to isolate the isopropoxide from the crystals were unsuccessful.

If 23 parts of sodium are dissolved at 100° in a mixture of 300 parts of isopropyl alcohol and 500 parts of crystallisable benzene, and the liquid is heated at 130—135° in a current of hydrogen, the alcohol is removed with the benzene, and sodium isopropoxide remains as a white powder, which is very hygroscopic. C. H. B.

Decomposition of Ethereal Nitrates by Alkaline Solutions. By W. G. Mixter (*Amer. Chem. J.*, **13**, 507—514).—In attempting to extract the cellulose in guncotton by converting it into substances capable of reducing alkaline copper tartrate, it was found that guncotton and similar ethereal nitrates themselves exert a direct reducing action on this solution. In order to trace the course of this reaction, experiments were instituted on the nitrates of ethyl, ethylene, glycerol, mannitol, and cellulose.

Ethyl nitrate is completely hydrolysed by alcoholic potash, as was observed by Millon (*Ann. Chim. Phys.* [3], **8**, 236), no other products being formed, and it does not reduce alkaline copper tartrate.

Ethylene nitrate is not merely hydrolysed by potash, as stated by Champion (*Compt. rend.*, **73**, 571), but is oxidised to carbonic anhydride at the expense of the nitric acid, both in aqueous and alcoholic solutions. It is oxidised to oxalic acid by boiling aqueous barium hydroxide, and does not reduce alkaline copper tartrate.

Glyceryl trinitrate is decomposed by hot aqueous potash into oxalic acid, carbonic anhydride, nitrous acid, ammonia, and traces of cyanogen and glycerol. Other organic substances appear to be formed, but could not be isolated. Glycerose is not formed. Glyceryl trinitrate reduces alkaline copper tartrate, but the products of decomposition to which the reduction is due are themselves decomposed by the further action of the alkali, since a solution of the nitrate in potash has no reducing power. On boiling glyceryl trinitrate with baryta-water, however, ammonia is expelled, and a reddish precipitate thrown down, which reduces alkaline copper tartrate, gives off ammonia when heated with lime, and consists of a mixture of barium oxalate with other unspecified substances. Nitrous acid is also formed in the reaction.

When mannitol nitrate is boiled with baryta-water, it yields a red, granular precipitate, which contains barium oxalate, and reduces alkaline copper tartrate. The nature of the reducing substance was not ascertained. The filtrate from the precipitate contains nitrites and organic matter, but does not reduce alkaline copper tartrate. Mannitol nitrate is decomposed by hot concentrated aqueous potash into oxalic acid and carbonic anhydride, and the solution has no reducing power. With dilute alkalis, however, oxalic acid is not formed, and the solution reduces alkaline copper tartrate, as the nitrate itself does.

Commercial pyroxylin or cellulose tetranitrate is decomposed by hot concentrated aqueous potash into carbonic anhydride, oxalic acid, and other substances, the nature of which was not ascertained. Sugar does not seem to be formed. A solution of pyroxylin in dilute aqueous potash reduces alkaline copper tartrate, and the substance itself dissolves in the copper solution and gradually reduces it.

The reducing action of cellulose hexanitrate is not so powerful as that of the tetranitrate.

The products of the action of nitric acid on pinitol, wood-fibre, gum arabic, gum tragacanth, balsam of Tolu, glycogen, starch, and cane sugar reduce alkaline copper tartrate, whilst those resulting from blood-albumin, egg-albumin, egg-yolk, caoutchouc, tartaric acid, beeswax, and tallow do not do so. Jn. W.

Cellulose. By C. F. Cross and E. J. Bevan (*Chem. News*, **65**, 77—78).—The authors give a few interim notes in connection with points they have under investigation. The precipitates of cotton cellulose hydrates from its solutions in ammoniocupric reagent or in $ZnCl_2$,HCl are soluble in solutions of alkali hydroxides, and the resulting solutions, when shaken with benzoic chloride, yield a white, curdy precipitate, which, after purification by solution in glacial acetic acid, &c., has the composition of a dibenzoate, $C_6H_8O_3(OBz)_2$. This is soluble in acetic anhydride, and on boiling the solution with fused sodium acetate, what appears to be a triacetyl monobenzoate is formed. A monobenzoate is likewise formed when cellulose soaked in aqueous soda (containing 15 per cent. Na_2O) is shaken with benzoic chloride. Moreover, the authors have obtained large quantities of acetic acid by fusing cellulose with alkali hydroxides at 300—400°. Taking into consideration these and many other facts now known about cellulose, the authors are inclined to assume that cotton cellulose is an anhydro-aggregate of unit groups for which they adopt a C_{12} formula, and in which 8 oxygen atoms are accepted as hydroxylic and two as carbonylic. Lignocelluloses, on the other hand, are regarded as anhydro-aggregates of 1, a cellulose allied to cotton and linen cellulose; 2, a penta-cellulose yielding furfuraldehyde and acetic acid on hydrolysis; 3, a, C_{18}-quinone or quinol, converted by chlorination and reduction into derivatives of the trihydric phenols, and comprising groups of the general form

$$CO<\begin{matrix}C(OH)_2\cdot C(OH)_2\\ CH=\!=\!=\!=CH\end{matrix}>CH_2.$$

Any final adoption of the proposed additions to the terminology of this group of plant constituents is regarded as premature.

D. A. L.

Aliphatic Stereoisomeric Glyoximes. By A. Hantzsch (*Ber.*, **25**, 705—712).—The glyoxime, $C_2H_4(NOH)_2$, appears to be capable of existing in one modification only, and its diacetyl derivative (m. p. 126°) is only partially decomposed into cyanogen, hydrogen cyanide, and carbonic anhydride by alkalis, so that although it is probable that it is antiglyoxime, $\begin{matrix}H\cdot C\cdot C\cdot H\\ \|\ \ \|\\ OH\cdot N\ N\cdot OH\end{matrix}$, this cannot be determined with certainty. Methyl- and dimethyl-glyoximes behave in much the same manner, and neither in the free state nor in that of diacetyl derivatives can they be converted into dimethylazoxazole by dehydration.

Chloramphiglyoxime, $\begin{matrix}Cl\cdot C & ——\ C\cdot H\\ \|\ \ & \ \ \|\\ N\cdot OH & N\cdot OH\end{matrix}$, identical with that of Naegeli, is obtained when chloral hydrate (1 mol.) is added to a solution of

sodium carbonate (1·5 mols.) and hydroxylamine hydrochloride (3 mols.); after remaining for four hours, sodium hydroxide (4 mols.) is added to the cooled solution, and on carefully acidifying, the compound separates, the remaining portion being obtained by extracting the filtrate with ether. It crystallises from water in silky needles containing 1 mol. H_2O, melts at 114°, resolidifies above this, and decomposes at 150°, and is sparingly soluble in cold water, readily in hot water, ether, and alcohol; concentrated alkalis decompose it, but it dissolves unchanged in dilute alkalis and ammonia. The *ammonium* salt separates in small prisms when ammonia is passed into an ethereal solution of the glyoxime; the *diacetyl derivative* crystallises in tables, melts at 114°, and is sparingly soluble in alcohol and ether.

Chlorantiglyoxime, $\begin{matrix} Cl\cdot C & - & C\cdot H \\ \| & & \| \\ OH\cdot N & & N\cdot OH \end{matrix}$, produced by passing dry hydrogen chloride into an ethereal solution of the last-described glyoxime, crystallises in small, anhydrous, nodular aggregates, melts at 161° with decomposition, and resembles its isomeride in solubility; it dissolves in alkalis with a yellow colour, and in concentrated ammonia with explosion due to the formation of ammonium hypochlorite. Very dilute alkalis dissolve it, and the amphi-modification separates on acidifying the solution. The *diacetyl* derivative is obtained from chlorantiglyoxime and acetic anhydride, as well as when dry hydrogen chloride is passed through an ethereal solution of diacetylchloramphiglyoxime; it resembles the latter in form and solubility, and melts at 90·5°.

Acetylchlorantiglyoxime, $\begin{matrix} Cl\cdot C & - & C\cdot H \\ \| & & \| \\ OH\cdot N & & N\cdot OAc \end{matrix}$ (?), is formed from chlorantiglyoxime and acetic anhydride, and also when either of the above-described chloroglyoximes is treated in the cold with acetic chloride; it melts at 163°, and is readily soluble in alcohol and ether.

A. R. L.

Condensation of Chloral with Paraldehyde and Ketones. By W. Koenigs (*Ber.*, **25**, 792—802).—*Chloralacetone*,

$$CCl_3\cdot CH(OH)\cdot CH_2\cdot COMe,$$

is prepared by heating acetone (3·2 grams) with chloral (8 grams) and glacial acetic acid (8 grams) in a sealed tube for 15 hours at 100°; the product is mixed with water, well shaken with dilute soda, and extracted with ether, the ether is removed, the residue dissolved in hot water, filtered, and again treated with ether; this is evaporated, and the residue crystallised from light petroleum; it melts at 75—76°, sublimes on cautiously heating, and is readily soluble in alcohol. The yield is 50 per cent. of the acetone employed. The same compound is also obtained by heating chloral with acetone at 150°.

On boiling chloralacetone with soda, an acid is formed in small quantity, which is almost free from chlorine, and melts at about 123°.

Butylchloral also combines with acetone; the product crystallises from a mixture of ether and light petroleum, and melts at 111—114°; the yield is very small.

Chloralacetophenone, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot COPh$, is obtained from acetophenone (19·2 grams), chloral (24 grams), and glacial acetic acid (24 grams), by heating on the water-bath for 20 hours in a reflux apparatus; the product is treated with water, dissolved in ether, and precipitated with light petroleum; it crystallises from 60 per cent. alcohol, melts at 76—77°, and decomposes on heating; the yield is equal to that of the acetophenone employed. The compound is scarcely volatile with steam; it is very stable towards acids, but readily decomposes on treatment with alkalis, probably into benzoylacrylic acid; on heating with 1 per cent. potash, an acid free from chlorine is formed in small quantity; it melts at 125—127°.

Trichlorethylideneacetophenone, $CCl_3 \cdot CH{:}CH \cdot COPh$, is prepared by dissolving chloralacetophenone in about 9 parts of pure, concentrated sulphuric acid; after remaining over night at ordinary temperatures, the solution is well cooled and treated with water; the compound crystallises from 80 per cent. alcohol in almost colourless plates or prisms which melt at 102°. The same substance is obtained by heating chloral with acetophenone in a sealed tube at 150—160°; it is readily volatile with steam, and sublimes without decomposition on cautiously heating.

Butylchloral also yields a condensation product with acetophenone which crystallises from dilute alcohol and melts at 110°.

Butylchloralaldol, $CHClMe \cdot CCl_2 \cdot CH(OH) \cdot CH(CHO) \cdot CHMe \cdot OH$, is formed by heating paraldehyde with 4 parts of butylchloral for 6—7 hours at 140—150°; it is a viscid, oily liquid, insoluble in water, soluble in ordinary media, and volatile with steam; it decomposes on heating, and, on distillation over lime, gives a compound which is free from chlorine, melts at about 50°, and has an odour resembling that of diphenyl. The yield of aldol is 20 per cent. of the paraldehyde employed. The aldol does not combine with sodium hydrogen sulphite, but yields a crystalline hydroxime.

Chloralaldol is obtained by heating paraldehyde (2·4 grams) with chloral (8 grams) and glacial acetic acid (8 grams) in a sealed tube for 9—10 hours at 100°; the yield is very small; the analytical results do not agree very closely with the formula $C_6H_9Cl_3O_3$, probably on account of the partial oxidation of the compound.

No condensation product of camphor and chloral could be obtained.

The author discusses a number of syntheses accomplished by means of chloral, and refers particularly to the formation of inactive malic acid from chloral and malonic acid; he points out the general bearing of his work on the theory of the production of acids in fruits and vegetables: for although chloral itself does not occur in nature, the corresponding hydroxyl compound, glyoxylic acid, is frequently found. J. B. T.

Action of Bromine on the Higher Fatty Acids. By F. Krafft and A. Beddies (*Ber.*, **25**, 481—488).—When stearic acid is heated for three hours with bromine (1 mol.) at 130—140°, about half the stearic acid remains unaltered, and three-fourths of the bromine is evolved as hydrogen bromide. By converting the product into the barium salt

and extracting with ether, the barium salt of the bromo-acid is easily dissolved; the barium stearate remaining insoluble. On analysis, the barium salt gives numbers agreeing with the formula of barium bromostearylenate, $(C_{18}H_{32}BrO_2)_2Ba$. When suspended in alcohol, and treated with hydrogen chloride, a liquid ethereal salt is obtained which decomposes on distillation under diminished pressure, and, after three rectifications, distils at 225—227° under 13 mm. pressure, losing all its bromine as hydrogen bromide. The product so obtained yields, on hydrolysis, an acid which boils at 223—225° under 10 mm. pressure, melts at 47—48°, and, on analysis, gave numbers corresponding with those required for stearoleïc acid, $C_{18}H_{32}O_2$.

When palmitic acid is treated with bromine in the same way, half of it is recovered unaltered. The mixed acids are separated by means of the barium salts as described above. The barium salt of the bromo-acid has the formula $(C_{16}H_{28}BrO_2)_2Ba$; the ethyl salt decomposes on distillation with evolution of hydrogen bromide, and the product so obtained, when hydrolysed with alcoholic potash, yields an unsaturated acid. The latter boils at 212—213° under 12·5 mm., melts at 42°, and, on analysis, gave numbers agreeing with the formula of palmitoleïc acid, $C_{16}H_{24}O_2$. It is mixed with a small quantity of a substance melting at 70—71°.

Myristic and lauric acids behave in a similar way. The former yields a bromo-acid, of which the barium salt has the formula $(C_{14}H_{24}BrO_2)_2Ba$, and, when converted into ethyl salt, distilled, and hydrolysed, yields an acid of the formula $C_{14}H_{24}O_2$, which boils at 200—205° under 13 mm., melts about 36°, and contains a small quantity of an acid melting at 56—57°. The barium salt of the bromo-acid derived from lauric acid has the formula $(C_{12}H_{20}BrO_2)_2Ba$, and finally yields an acid $C_{12}H_{20}O_2$, which boils at 182—185° under 13 mm., melts at about 30°, and is mixed with a small quantity of an acid melting at 49—50°. E. C. R.

Alde-acids. By J. A. Wanklyn and W. Johnson (*Chem. News*, **65**, 75).—The authors have treated, severally, with alkaline permanganate, commercial valeric acid, palmitic acid prepared from palm oil, and margaric acid, commercially known as stearic acid. In the first instance, they have obtained a crystalline acid; in the second, an acid yielding a barium salt containing 21·31 per cent. of barium, the exact percentage required by barium aldepalmitate, whilst the barium salt of the palmitic acid employed contained 20·92 per cent. of the metal; and in the third instance, a new acid is obtained.

D. A. L.

Introduction of Acid Radicles into Ethyl Acetoacetate. By H. v. Pechmann (*Ber*, **25**, 410—411).—The author finds that acid chlorides and anhydrides react with ethyl acetoacetate in alkaline solution with the displacement of 1 or 2 atoms of hydrogen by the acid radicle; for example, ethyl acetoacetate, when shaken with sodium hydroxide and an excess of benzoic chloride, yields ethyl dibenzoylacetoacetate, ethyl benzoylacetoacetate, and unaltered ethyl acetoacetate. Ethyl benzoylacetate, acetone dicarboxylate, and 1 : 3-diketones behave in a manner similar to ethyl acetoacetate.

A. R. L.

Haloïd Derivatives of Ethyl Acetoacetate. By A. Haller and A. Held (*Compt. rend.*, **114**, 398—401).—Ethyl monochloroacetoacetate, obtained by direct chlorination, when freshly prepared, yields *ethyl amidomethylthiazolecarboxylate* when treated with thiocarbamide under the conditions described by Zurcher. A similar result was obtained with some of the compound that was a year old. The freshly-prepared compound with potassium cyanide yielded as much as 25 per cent. of the γ-cyano-derivative; whereas the old preparation yielded a very small quantity of the γ-derivative. It would seem that ethyl monochloroacetoacetate, obtained by direct chlorination, undergoes a change in constitution with lapse of time.

Ethyl monobromacetoacetate, obtained by Duisberg by direct bromination, yields only ethyl α-amidothiazylacetate by condensation with carbamide without any trace of the isomeride; when treated with potassium cyanide, it yields ethyl succinosuccinate without any trace of ethyl γ-cyanacetoacetate or the α-derivative. The constitution of Duisberg's product is still uncertain.

These results seem to indicate that, according to their mode of formation and the nature of the reactions in which they take part, the monhaloïd derivatives of ethyl acetoacetate behave sometimes as α-derivatives, sometimes as γ-derivatives, sometimes as a mixture of both. C. H. B.

Constitution of Ethyl Chloracetoacetate. By A. Hantzsch and H. Schiffer (*Ber.*, **25**, 728—732).—By the synthesis of ethyl amidomethylthiazolecarboxylate from ethyl chloracetoacetate and thiocarbamide, and that of ethyl amidothiazylacetate from ethyl bromacetoacetate, Hantzsch and also Steude were led to believe that the chloro-compound is an α-, and the bromo-compound a γ-derivative. Haller and Held obtained, however, a mixture of α- and γ-cyano-derivatives by treating the chloro-compound with potassium cyanide (preceding abstract). The authors find that ethyl amidomethylthiazolecarboxylate is formed in almost theoretical yield from ethyl chloracetoacetate as above. When ethyl dimethylacetoacetate is treated with sulphuryl chloride, a chloro-derivative decomposing at 210—215° is obtained, which, when heated in dilute alcoholic solution with thiocarbamide, gives *ethyl amidothiazylisobutyrate*, $COOEt\cdot CMe_2\cdot C\begin{matrix}CH\cdot S\\ \|\\ N{=}C\cdot NH_2\end{matrix}$, melting at 137°, and is, therefore, a γ-chloro-derivative,

$$CH_2Cl\cdot CO\cdot CMe_2\cdot COOEt.$$

The authors, therefore, conclude that ethyl chloracetoacetate is an α-derivative, and that the action of potassium cyanide on it is not a normal one. They further confirm the above mentioned statement that ethyl bromacetoacetate is a γ-derivative and not, as supposed by Nef, a mixture of α- and γ-derivatives. A. R. L.

Allylethylsuccinic and Allylmethylsuccinic Acids. By E. Hjelt (*Ber.*, **25**, 488—491).—Ethyl allylbutenyltricarboxylate is first prepared from ethyl butenyltricarboxylate, allyl iodide, and sodium, or from ethyl allylmalonate, ethyl bromobutyrate, and sodium. The portion of the product boiling at 282—291° is hydrolysed with potash

and the solution acidified with hydrochloric acid; allyl ethyltricarboxylic acid is obtained; it melts at 123°, and when heated at 150° yields two allylethylsuccinic acids. The sparingly soluble *parallylethylsuccinic acid* crystallises in rhombic plates, melts at 163—166°, and dissolves in 110 parts of water at 20°. *Mesoallylethylsuccinic acid* crystallises in small tablets, melts at 108—111°, and dissolves in 37 parts of water. The para-acid dissolves easily in acetic chloride, and is precipitated unchanged on the addition of water; when heated above its melting point, it is converted into the anhydride, from which the meso-acid mixed with a small quantity of the para-acid is obtained by treatment with water. The meso-acid is easily converted into the anhydride, from which it is regenerated by the action of water; it cannot be converted into the para-acid by heating with hydrochloric acid.

Ethyl allylpropenyltricarboxylate is prepared from ethyl propenyltricarboxalate, allyl iodide, and sodium, and is hydrolysed with potash; on acidifying the solution, allylmethyltricarboxylic acid is obtained; it melts at 140°, and, when heated at 150°, yields two allylmethylsuccinic acids. *Parallylmethylsuccinic acid* melts at 147—148°, crystallises in prisms, is sparingly soluble in water, and when heated at 170°, yields the anhydride, which is converted by water into the meso-acid. The silver, copper, barium, and calcium salts are described. *Mesoallylmethylsuccinic acid*, melts at 86—87°, crystallises in small needles, and dissolves in 27 parts of water. E. C. R.

Dimethylracemic Acid. By C. Böttinger (*Ber.*, **25**, 397—398).—The author confirms Zelinsky's observation (this vol., p. 430) that the acid obtained by him from pyruvic acid is identical with Fittig, Daimler, and Keller's dimethylracemic acid (Abstr., 1889, 491); the following is an improved method of preparing it. Pyruvic acid (10 c.c.) is dissolved in absolute alcohol (140 c.c.) and allowed to remain at the ordinary temperature for three days in contact with freshly prepared granulated zinc; the liquid is then poured off, and after drying the zinc, the coating of salt is mechanically removed, dissolved in water, treated with hydrogen sulphide, the solution evaporated, and the residue converted into the ammonium salt, from the aqueous solution of which, on adding calcium chloride, calcium dimethylracemate (0·9 gram) separates. The acid prepared from the latter salt contains 1 mol. H_2O, and melts at 177—178°; its further investigation is being carried on by Fittig. A. R. L.

New Method of Preparing Aliphatic Hydroxamic Acids. By A. Miolati (*Ber.*, **25**, 699—701).—Aliphatic hydroxamic acids are obtained when dry hydroxylamine hydrochloride is boiled in a reflux apparatus with an acid anhydride (rather more than 2 mols.) for about an hour; the cold solution is neutralised with sodium carbonate, excess of copper acetate added, and the basic copper salt which separates is dried, suspended in alcohol, and decomposed by a current of hydrogen sulphide; the hydroxamic acid is isolated from the alcoholic filtrate by evaporation. As the solution, before being neutralised by sodium carbonate, does not give a precipitate with

copper acetate, it seems probable that it then contains (in the case of the acetic derivative) the compound OAc·CMe:NOH (compare next abstract). The author obtained C. Hoffmann's acetohydroxamic acid (Abstr., 1890, 127), and *propionohydroxamic acid*,

$$CH_2Me{\cdot}C(OH):NOH,$$

by this method; the latter forms transparent prisms, melts at 85°, and is insoluble in ether and benzene, but readily soluble in water and alcohol. *Formohydroxamic acid*, OH·CH:NOH, is prepared by boiling anhydrous formic acid with hydroxylamine hydrochloride. A detailed description of several of these compounds will appear later in the *Gazzetta*. A. R. L.

Action of Hydroxylamine on Chloral. By A. Hantzsch (*Ber.*, **25**, 701—705; compare Naegeli, Abstr., 1883, 728; V. Meyer, Abstr., 1891, 1181).—The additive compound, *chloralhydroxylamine*, $OH{\cdot}CH(CCl_3):NH{\cdot}OH$, is obtained by triturating chloral hydrate and sodium carbonate (1 mol. of each) with hydroxylamine hydrochloride (1 mol.), dissolving the mass in a little water, extracting with ether, and crystallising the crude substance from benzene or chloroform; when pure, it forms lustrous scales, melts at 98°, is readily soluble in ether and alcohol, less so in water, and is odourless. It gives no precipitate with silver nitrate, decomposes into trichloraldoxime, hydroxylamine hydrochloride, and other compounds on keeping, gives chloroform when heated with alkalis, and when its aqueous solution is evaporated, chloral is volatilised and hydroxylamine hydrochloride remains; the latter is also precipitated from an ethereal solution of the compound by hydrogen chloride or acetic chloride. *Diacetohydroxamic acid*, OH·CMe:NOAc, is formed when the compound is dissolved in acetic anhydride, and the solution evaporated in a vacuum; it crystallises in white needles, melts at 89°, and dissolves readily in water, forming a solution which only gives a precipitate with copper acetate and a dark-red coloration with ferric chloride when heated with these reagents, due to its decomposition into acetohydroxamic acid (compare preceding abstract). A. R. L.

Oximidoacetic Acid. By C. Cramer (*Ber.*, **25**, 713—721).—*Oximidoacetic acid*, NOH:CH·COOH, is obtained when crude, syrupy glyoxylic acid, prepared by heating dibromoacetic acid at 140° with water, and evaporating the product on a water-bath, is mixed with a concentrated solution of hydroxylamine hydrochloride, and the mixture extracted, after a time, with ether. It crystallises from alcohol in colourless needles containing 1 mol. H_2O; the crystals effloresce over concentrated sulphuric acid, and the anhydrous substance thus produced melts at 137—138° with decomposition; it is readily soluble in water and alcohol, less so in ether, and insoluble in cold benzene. Its aqueous solution decomposes into water, carbonic anhydride, and hydrogen cyanide, when heated at 120°; on boiling it with barium hydroxide, barium carbonate is formed, but it is not decomposed by hot concentrated hydrochloric acid. The solution neutralised with ammonia gives, with silver and mercurous nitrates, white precipitates,

but not with lead, calcium, and barium salts. Experiments to determine if the acid exists in stereoisomeric forms yielded negative results. When dry hydrogen chloride is passed through an ethereal solution of the acid, it is unaltered, as also when it is dissolved in acetic chloride; on gently warming it with acetic anhydride, it dissolves, but the product could not be purified.

Ethyl oximidoacetate, NOH:CH·COOEt, prepared by heating the silver salt with ethyl iodide, is a heavy oil, which commences to decompose a little above 100°, and is easily soluble in alcohol, ether, and benzene; water also dissolves it, and it is readily hydrolysed by alkalis. These characteristics and a direct comparison have proved that it is not identical with the compound obtained by Pröpper from ethyl acetoacetate and nitric acid (*Annalen*, **222**, 48), and attempts to convert one into the other by treatment with hydrogen chloride in ethereal solution were unsuccessful. When fuming nitric acid is added to ethyl oximidoacetate, Pröpper's compound is obtained; it has the constitution $\begin{matrix}\text{COOEt·C:N·O}\\ \text{COOEt·C:N·O}\end{matrix}$, and is, consequently, produced from 2 mols. of the oximidoacetate with the elimination of 2 mols. H_2O; the sodium and ammonium derivatives described by him are additive compounds of this with the respective hydroxides. The compound obtained by Pröpper from ethyl chloracetoacetate is, as described by him, ethyl chloroximidoacetate. A. R. L.

Imidosulphonic Acids. By F. Krafft and E. Bourgeois (*Ber.*, **25**, 472—477).—Imidosulphonic acids may be prepared by the condensation of amidosulphonic acid with organic substances.

Amidosulphonic acid, $NH_2·SO_3H$, is prepared by saturating a concentrated solution of hydroxylamine hydrochloride with sulphurous anhydride, and keeping the solution saturated for two or three days by means of a slow current of the same gas. It is purified by crystallisation from slightly warm water, but is easily converted, by heating with water, into acid ammonium sulphate, as it is also by heating in damp air at 130—140°. The *barium* salt is characteristic, and is obtained by cautiously digesting the acid solution with barium carbonate, and concentrating the filtrate in a vacuum with the aid of a gentle heat, or it may be obtained in slender, lustrous needles, by adding alcohol to the aqueous solution. Amidosulphonic acid combines with alcohols to form ammonium alkyl sulphates.

Ammonium ethyl sulphate is obtained when finely-powdered amidosulphonic acid is dissolved in absolute alcohol by gently boiling the mixture for three or four hours. It forms colourless, transparent crystals, is very hygroscopic, dissolves easily in water, more sparingly in absolute alcohol, is insoluble in dry ether, and absorbs water from wet ether to form oily drops. It gives up its water over sulphuric acid, and when dry melts at 99°. The dry salt decomposes above its melting point into acid ammonium sulphate and ethylene, and at 210—220° the latter is evolved in a regular stream.

Ammonium methyl sulphate, obtained in a similar way, forms hygroscopic leaflets, melts at 135°, and is precipitated from its solution in methyl alcohol by ether.

Ammonium isobutyl sulphate is precipitated by ether, forms colourless, slightly hygroscopic leaflets, and melts at 215° with evolution of isobutylene.

Benzenylimidosulphonic acid, $CH{\cdot}Ph{:}N{\cdot}SO_3H$, is obtained by heating amidosulphonic acid (5 parts) with pure benzal chloride (8·5 parts) in an oil-bath at 110°, heating the condensation product thus formed at 125—130° under 100 mm. pressure, then under 15 mm. pressure, and, finally, at 140—150°. It is obtained as a solid, yellow mass, which slowly absorbs moisture from the air, and decomposes. When obtained in this way, it is mixed with 2·5 per cent. of chloride and a small quantity of acid ammonium sulphate and resin, but cannot be further purified. It is easily decomposed by water at 0°, and forms benzaldehyde and amidosulphonic acid.

A similar decomposition is observed in the case of the compound of the empirical formula $(MeCN)_2,SO_3,H_2O$, obtained by treating acetonitrile with fuming sulphuric acid, and which decomposes in damp air yielding diacetamide and amidosulphonic acid.

A dimethylmethylenimidosulphonic acid, $CMe_2{:}N{\cdot}SO_3H$, is obtained as a crystalline precipitate on passing a current of sulphurous anhydride into an alcoholic solution of acetoxime. When warmed with water, it is decomposed into acetone and amidosulphonic acid.

E. C. R.

Alkyl Derivatives of Isosuccinimide. By W. J. Comstock and H. L. Wheeler (*Amer. Chem. J.*, **13**, 520—525).—When silver succinimide is treated with alkyl iodides, alkyl succinimides are obtained, which are isomeric with those of the class represented by the ethylsuccinimide prepared by Landsberg from sodium succinimide (Abstr., 1883, 477), and are distinguished from them by yielding a succinamidine when treated with aniline (compare Menschutkin, *Annalen*, **162**, 170; Comstock and Kleeberg, Abstr., 1890, 1414). *Ethylisosuccinimide*, $\begin{matrix}CH_2\text{——}CO\\ |\\ CH_2{\cdot}C(OEt)\end{matrix}\!\!>\!N$, is formed, together with a small amount of ethylsuccinimide, $\begin{matrix}CH_2{\cdot}CO\\ |\\ CH_2{\cdot}CO\end{matrix}\!\!>\!NEt$, when dry silver succinimide (1 mol.) is digested with ethyl iodide (1 mol.) in chloroform solution (2 or 3 vols.) for several weeks at the ordinary temperature. On purification, it is obtained as a colourless oil, boiling with slight decomposition at 144—146° under a pressure of 20 mm. It reacts with aniline to form phenylsuccinamidine (see below), and is reconverted into succinimide by exposure to moist air. *Propylisosuccinimide* is prepared in a similar manner. It boils at 153—154° under a pressure of 19 mm., and reacts in a similar way with aniline. A small amount of *propylsuccinimide*, $\begin{matrix}CH_2{\cdot}CO\\ |\\ CH_2{\cdot}CO\end{matrix}\!\!>\!NPr^{\alpha}$, is likewise formed at the same time, but the latter is best prepared by distilling hydrogen propylamine succinate, after Menschutkin's method of preparing the methyl and ethyl compounds. It is a colourless oil, which boils at 247—248° under 763 mm. pressure, at 136—137° under 20 mm. pressure, and solidifies at 15—16°. It does not react with aniline.

Succinimide thus resembles formanilide and other formyl derivatives of aromatic amines in the behaviour of its silver and sodium derivatives with alkyl iodides (this vol., p. 707); but the assumption that silver and sodium succinimides are different in constitution is hardly tenable in this case, seeing that both normal and iso-succinimides can be obtained from the former salt, and that it is hardly likely that a tautomeric change would take place at the ordinary temperature.

Phenylsuccinamidine, $\begin{matrix}CH_2\text{———}CO\\ |\\ CH_2\cdot C(NHPh)\end{matrix}\!\!>\!N$, is formed by adding aniline to either of the above isosuccinimide derivatives. It is soluble in hot alcohol, crystallises from that solvent in small, transparent, quadrilateral plates, and melts at 216°. The *aurochloride* forms a voluminous precipitate of sulphur-yellow, microscopic needles when prepared in the cold, but crystallises in gold-coloured prisms when allowed to separate from a hot solution. It melts with decomposition at 170°. Jn. W.

Thiocarbamides, Cyanocarbamides, and Cyanothiocarbamides. By O. Hecht (*Ber.*, **25**, 813—823; compare Abstr., 1891, 476 and 1103).—*Symmetrical methylisobutylthiocarbamide*,

$$NHMe\cdot CS\cdot NH\cdot C_4H_9,$$

is prepared from isobutylamine and methylthiocarbimide; it crystallises from water in colourless, lustrous plates, melts at 77·5°, and is extremely soluble in acetone or chloroform. *Symmetrical ethylisobutylthiocarbamide*, $NHEt\cdot CS\cdot NH\cdot C_4H_9$, melts at 77·5°, and is obtained in a manner similar to the preceding compound, which it closely resembles. *Symmetrical allylisobutylthiocarbamide*,

$$C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_4H_9,$$

prepared from allylthiocarbimide and isobutylamine, is somewhat unstable, and crystallises with difficulty; it melts at 28·5°. *Symmetrical isobutylphenylthiocarbamide*, $C_4H_9\cdot NH\cdot CS\cdot NHPh$, formed from isobutylamine and phenylthiocarbimide, crystallises from water in colourless needles, and melts at 82°.

Symmetrical propylpentenethiocarbamide, $C_3H_7\cdot NH\cdot CS\cdot N{:}C_5H_{10}$, is prepared from propylthiocarbimide and piperidine; it crystallises from alcohol in tetragonal pyramids, $a : c = 1 : 0{\cdot}5488$, melts at 75°, and reacts with mercuric oxide and ammoniacal silver solution on warming. A more sparingly soluble bye-product is obtained in the preparation of the carbamide; it contains 27 per cent. of sulphur, crystallises from alcohol in small, lustrous plates, and melts at 167° with decomposition. The observations of Dixon (Trans., 1891, 551) and of Salkowski (Abstr., 1891, 1474) on the thiocarbamide derivatives of benzylamine and benzylthiocarbimide are confirmed. Symmetrical ethylbenzylthiocarbamide may be prepared from benzylthiocarbimide and ethylamine, whilst symmetrical allylbenzylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_7H_7$, is formed by the mutual action of allylthiocarbimide and benzylamine.

Ethylcarbamine cuprocyamide, $[NHEt\cdot CO\cdot N(CN)]_2Cu + 5H_2O$, is

prepared from the corresponding sodium salt by the addition of cupric sulphate, and is already known. *Allylcarbaminesodiocyamide*, $C_3H_5{\cdot}NH{\cdot}CONa{\cdot}CN$, is prepared by adding allyl isocyanate to sodium cyanamide in absolute alcohol; it is amorphous, and melts at 246° with decomposition. The *cupro-derivative*,

$$C_3H_5{\cdot}NH{\cdot}CO{\cdot}N(CN){\cdot}Cu{\cdot}OH,$$

is precipitated as a green powder on the addition of cupric sulphate solution to the preceding compound.

Phenylthiocarbamineisobutylcyamide, $NHPh{\cdot}CS{\cdot}N(CN){\cdot}C_4H_9$, is obtained by heating phenylthiocarbaminesodiocyamide, from phenylthiocarbimide and sodium cyanamide, with isobutyl iodide; it crystallises from alcohol in colourless, slender needles, and melts at 139°; the compound is not decomposed by heating with mercuric oxide or silver nitrate. J. B. T.

Thiobiurets. By O. Hecht (*Ber.*, **25**, 749—758).—Thiobiuret, $C_2H_5N_3OS$, was first obtained by Wunderlich (Abstr., 1886, 435), and is prepared by digesting silver cyanocarbamide (1 mol.) with an aqueous solution of sodium chlorate (1 mol.), filtering, adding an equivalent quantity of ammonium chloride and ammonia, and passing hydrogen sulphide through the boiling solution, the ammonia being from time to time renewed; the compound separates from the filtrate in long, stout, transparent needles, containing 1 mol. H_2O, and when dried at 100° is anhydrous and melts at 186°; it is readily soluble in alcohol, sparingly in chloroform, slightly in ether, and insoluble in light petroleum. The yield is small.

α-Methylthiobiuret, $NHMe{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, is obtained in small quantity by mixing methylcarbimide with sodium cyanamide in molecular proportion, when the additive compound $NHMe{\cdot}CO{\cdot}NNa{\cdot}CN$ is formed, dissolving this in water, and treating it as above described with ammonium chloride, ammonia, and hydrogen sulphide; it forms lustrous needles, melts at 194° with decomposition, has a very bitter taste, and resembles the ethyl derivative (see below) in solubility and reactions.

α-Ethylthiobiuret, $NHEt{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, is prepared from ethylcarbimide in a manner similar to the methyl compound; the yield is 60 per cent. of the theoretical; it crystallises in long, thin, transparent prisms, melts at 184° with the evolution of gas, has a very bitter taste, and is readily soluble in alcohol and hot water, very sparingly in ether, and insoluble in light petroleum. It dissolves in ammonia and in hydrochloric acid; its aqueous solutions give with copper sulphate a white precipitate, dissolving in potassium hydroxide to a red solution, from which sulphur separates on heating; with ammoniacal silver nitrate in the cold, and with mercuric oxide on heating, it gives precipitates of the sulphides, but it only reacts slowly and partially when heated with alkaline lead salts; silver nitrate, mercuric chloride, and lead acetate give white precipitates.

α-Methyldithiobiuret, $NHMe{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, is produced by mixing an alcoholic solution of cyanamide (6 grams) and sodium (3·3 grams) with methylthiocarbimide (10·6 grams), evaporating the alcohol,

dissolving in water, and treating the solution with ammonium chloride, ammonia, and hydrogen sulphide. It crystallises from water in colourless, delicate, silky needles, melts at 153° with decomposition, tastes bitter, and gives the biuret reaction with copper sulphate and alkali.

α-Ethyldithiobiuret, $NHEt{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, is obtained from ethylthiocarbimide, the yield being 59 per cent. of the theoretical; it crystallises in lustrous, white needles, melts at 175° with decomposition, and is very sparingly soluble in cold water; its aqueous and alcoholic solutions give the biuret reaction.

α-Propyldithiobiuret, $NHPr^{\alpha}{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, prepared from propylthiocarbimide, is a white, crystalline powder, and melts at 121° without decomposition.

α-Allyldithiobiuret, $C_3H_5NH{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, is prepared from allylthiocarbimide; it crystallises in small needles and melts at 138°.

α-Phenyldithiobiuret, $NHPh{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, has been prepared by Wunderlich, and is obtained from phenylthiocarbimide; it melts at 174° with decomposition, and differs principally from the aliphatic analogues in having less affinity for combining with acid.

A. R. L.

Metadinitrobenzene. By C. Willgerodt (*Ber.*, **25**, 608—609).—When metadinitrobenzene is treated with alcoholic stannous chloride, or boiled with zinc-dust in alcoholic solution, it yields the symmetrical metadinitroazoxybenzene previously obtained by Klinger and Pitschke (Abstr., 1886, 53). It is almost white when pure, melts at 145°, and dissolves in nearly all organic solvents.

Metadinitrobenzene gives no coloration with alkalis when free from dinitrothiophen; the latter may be separated by dissolving in alcohol, warming with an excess of soda, precipitating with water, washing the precipitate until almost colourless, and recrystallising from alcohol. It is then almost white, melts at 91° (uncorr.), and, as stated before, gives no coloration with alkalis; with acetone in alkaline solution, it still gives the beautiful, violet coloration observed by Janovsky (Abstr., 1891, 685). H. G. C.

Reduction of Metabromonitrophenol. By F. W. Schlieper (*Ber.*, **25**, 552—555).—Metabromonitrophenol is prepared by treating finely-powdered nitrophenol with twice the theoretical quantity of bromine for several days at the ordinary temperature; the product is washed with water, crystallised several times from concentrated hydrochloric acid, and finally from a mixture of benzene and light petroleum; it melts at 147—148°, not at 110°, as stated by Pfaff. By the action of stannous chloride (5·5 grams) on the phenol (1·3 grams), metamidophenol is obtained together with bromamidophenol, the relative quantities depending on the proportion of stannous chloride employed and on experimental conditions.

Bromonitrophenetoïl may be prepared by the mutual action of bromonitrophenol, sodium ethoxide, and ethyl iodide; on reduction, it also yields ethoxyamidobenzene [1 : 3] as chief product, together with some of the corresponding bromo-derivative.

The above results reconcile the contradictory statements of Pfaff and Lindner on this subject. J. B. T.

Amidine Picrates. By W. Dieckmann (*Ber.*, **25**, 546—547).—*Formamidine picrate*, $NH{:}CH{\cdot}NH_2,C_6H_2(NO_2)_3{\cdot}OH$, is obtained by adding formamidine hydrochloride to picric acid in aqueous solution, and crystallises in long, lustrous, yellow needles melting at 248°. *Acetamidine picrate*, $NH{:}CMe{\cdot}NH_2,C_6H_2(NO_2)_3{\cdot}OH$, is deposited in long, flat needles or in lustrous scales, and melts at 245°. *Benzenylamidine picrate* crystallises in yellow needles melting at 228°.

J. B. T.

Conversion of Aromatic Amines into Chlorine Derivatives of the Hydrocarbons. By Prud'homme and C. Rabaut (*Compt. rend.*, **114**, 362—364).—Sandmeyer has shown that when the chlorides of the diazo-compounds formed by the amines of the benzene series are heated with an acid solution of cuprous chloride, they yield chloroderivatives of the corresponding hydrocarbons, and Möhlau showed that nitrates of the amines are directly converted into diazo-derivatives by the action of zinc powder and hydrochloric acid. The authors find that these two reactions can be combined by treating the nitrates of the amines with a solution of cuprous chloride.

When aniline nitrate is heated with a hydrochloric acid solution of cuprous chloride, nitrogen oxides are evolved, and the liquid when distilled yields chlorobenzene boiling at 132°, and paradichlorobenzene melting at 55° and boiling at 173°.

Cupric chloride yields no dichlorobenzene by its action on diazobenzene chloride. It converts the latter partially into monochlorobenzene. Chromic and ferric chlorides behave similarly. It follows that the production of dichlorobenzene must be attributed to the formation of paraphenylenediamine and its diazo-derivative during the reduction of the aniline nitrate.

Cuprous chloride in this reaction may be replaced by chromous chloride, but not by ferrous or stannous chloride. C. H. B.

Anilides, Isoanilides, and their Analogues. By W. J. Comstock and H. L. Wheeler (*Amer. Chem. J.*, **13**, 514—520).—The sodium and silver salts of form-α-naphthalide react in the same manner with methyl iodide as salts of other aromatic formyl compounds. *Silver form-α-naphthalide* (compare Gattermann, Abstr., 1890, 1112) separates as a voluminous, grey precipitate on gradually adding silver nitrate (1 mol.) in 50 per cent. alcoholic solution to an aqueous alcoholic solution of form-α-naphthalide (1 mol.) and sodium hydroxide. It is sensitive to light. *Methylisoform-α-naphthalide*, $C_{10}H_7{\cdot}N{:}CH{\cdot}OMe$, is obtained as a heavy oil by treating the dry silver salt with a solution of methyl iodide in dry ether. It has a fishy odour, and boils with decomposition at 306—308° under atmospheric pressure. Its behaviour towards water, dilute acids, and primary amines is similar to that of methylisoformanilide (Abstr., 1890, 1258 and 1414).

Gattermann (*loc. cit.*) having found two apparently tautomeric

modifications of nitroparacetoluidide, it was deemed likely that nitroformanilide might also exist in two such modifications, inasmuch as the sodium and silver salts behave towards methyl iodide as if they have the structures $NO_2 \cdot C_6H_4 \cdot NNa \cdot CHO$ and $NO_2 \cdot C_6H_4 \cdot N{:}CH \cdot OAg$ respectively. Both salts, however, yielded nitroformanilides identical n melting point and microscopic appearance. *Metanitroformanilide* is prepared by boiling metanitraniline with excess of anhydrous formic acid, and then adding water and recrystallising from hot water, alcohol, or benzene. It is sparingly soluble also in ether and light petroleum, forms microscopic tufts of hair-like, bent needles, and melts at 134°. *Sodium metanitroformanilide* is prepared by adding sodium methoxide, made from sodium (1 mol.) and dry methyl alcohol, to a pasty mixture of the nitroformanilide and methyl alcohol. It is readily soluble in methyl alcohol, but insoluble in dry ether, and, when thoroughly washed with the latter, is a lemon-yellow solid, but when crystallised from the former forms orange needles, and contains 1 mol. of alcohol of crystallisation. It is reconverted by water or carbonic anhydride into the nitroformanilide. *Methylmetanitroformanilide* is prepared by heating sodium metanitroformanilide with methyl iodide in a reflux apparatus or sealed tube (100°), until the mixture no longer shows an alkaline reaction. Carbonic anhydride and air must be excluded. It crystallises from alcohol in long, yellowish needles, and melts at 70—71°. The methyl metanitraniline prepared from the anilide melted at 67°, and its nitrosamine at 76° (compare Nölting and Strecker, Abstr., 1886, 544). *Silver metanitroformanilide* is prepared in the same manner as silver formanilide (Abstr., 1890, 1258 and 1414). It is a colourless, amorphous solid, insoluble in hot water. *Methylmetanitroisoformanilide* is prepared by treating the dry silver salt with methyl iodide in ethereal solution. It crystallises in long, slender, pale-yellow needles, melts at 45°, and boils at 172—173° under a pressure of 21 mm. It is converted by dilute hydrochloric acid into metanitraniline hydrochloride.

The isoanilides react with aliphatic and aromatic secondary amines to form formamidines. *Di-α-naphthylformamidine*,

$$C_{10}H_7 \cdot N{:}CH \cdot NH \cdot C_{10}H_7,$$

is prepared by heating methylisoform-α-naphthalide with α-naphthylamine, and recrystallising the product from hot benzene. It crystallises in colourless plates, melts at 199°, dissolves in alcohol, ether, and benzene, but is insoluble in light petroleum and cold dilute mineral acids. *Phenyl-α-naphthylformamidine*, $C_{10}H_7 \cdot N{:}CH \cdot NHPh$, is prepared by treating methylisoform-α-naphthalide with aniline, and precipitating the benzene solution of the product with light petroleum. It melts at 142°, and is soluble in alcohol, ether, and benzene, but only sparingly in light petroleum. Its basic properties are much more strongly marked than those of the dinaphthyl compound. *Metadinitrodiphenylformamidine*, $NO_2 \cdot C_6H_4 \cdot N{:}CH \cdot NH \cdot C_6H_4 \cdot NO_2$, is prepared by slowly heating a mixture of methylmetanitroisoformanilide (1 mol.) and metanitraniline (1 mol.) to 110°, and recrystallising the solid product from alcohol. It forms small, yellow, hair-like needles,

melts at 195—196°, dissolves in alcohol, ether, chloroform, and acetone, but is insoluble in light petroleum. *Metanitrodiphenylformamidine*, $NO_2 \cdot C_6H_4 \cdot N{:}CH \cdot NHPh$, is prepared by mixing methylmetanitroisoformanilide (1 mol.) with aniline (1 mol.), and recrystallising the solid product from absolute alcohol. It crystallises in long, yellow prisms, and melts at 145°.

Diethylphenylformamidine, $NPh{:}CH \cdot NEt_2$, is prepared by boiling methylisoformanilide with a slight excess of diethylamine, in a reflux apparatus, for two hours. It is a colourless oil, boiling, with partial decomposition, at 273—275° under atmospheric pressure. The *aurochloride*, $C_{11}H_{16}N_2,HAuCl_4$, may be crystallised in small, lemon-yellow plates, by adding water to the alcoholic solution. It melts at 147°.

Methyldiphenylformamidine, $CHNPh{:}CH \cdot NMePh$, is prepared by distilling a mixture of methylaniline and methylisoformanilide which has been kept for some days at the ordinary temperature, and heated on the water-bath for a short time previous to the distillation. It is a heavy, yellowish oil, boiling at 214° under 22 mm. pressure. The *aurochloride* may be crystallised in gold-coloured plates by adding water to the alcoholic solution; it melts at 145°.

The isoanilides also react with cyanamide to form cyanogen derivatives of the formamidines. *Cyanophenylformamidine*,

$$NPh{:}CH \cdot NH \cdot CN,$$

separates as a crystalline crust when an ethereal solution of cyanamide and methylisoformanilide is kept for 24 hours at the ordinary temperature. It is insoluble in ether, but soluble in alcohol and water, crystallising from the former in long needles, and from the latter in long, flat, colourless prisms; it melts at 138°. *Cyanoparatolylformamidine*, $C_6H_4Me \cdot N{:}CH \cdot NH \cdot CN$, is prepared from cyanamide and methylisoformanilide in a similar way; it crystallises from alcohol in long prisms, and melts at 176—177°. Jn. W.

Derivatives of Aromatic Formyl Compounds. By W. J. Comstock and R. R. Clapp (*Amer. Chem. J.*, **13**, 525—528).—The sodium and silver derivatives of formorthotoluidide and formoparatoluidide, like those of formanilide (Comstock and Kleeberg, Abstr., 1890, 1414), yield methyl derivatives having different constitutions, the methyl in the first case being linked to nitrogen, in the other through oxygen to carbon. To complete the parallel, the toluidides prepared by various methods from the metallic derivatives were found to be identical, the isomerism thus existing only in the alkyl derivatives.

Silverformorthotoluidide and *formoparatoluidide*, $C_6H_4Me \cdot N{:}CH \cdot OAg$, are prepared in the same way as the formanilide (preceding abstract); the ortho-compound is amorphous, the para-compound crystalline (small needles), and both are insoluble in cold water, and sensitive to light. The methyl derivatives are prepared in the same way as the methyl formanilides (*loc. cit.*). *Methylisoformorthotoluidide*,

$$C_6H_4Me \cdot N{:}CH \cdot OMe,$$

is an oil boiling at 211—213° under 760 mm. pressure, and having an

aromatic odour. *Methylisoformoparatoluidide* is a similar oil, boiling at 216—218° under 761 mm. pressure. The amidines are prepared from the methyltoluidides by means of the toluidines, in the manner previously described (*loc. cit.*), thus proving the oxygen linkage of the methyl groups. Diorthotolylformamidine,

$$C_6H_4Me\cdot NH\cdot CH{:}N\cdot C_6H_4Me,$$

prepared also by Ladenburg (Abstr., 1878, 54) and Senier (Trans., 1885, 762), melts at 150°, and is soluble in alcohol. Diparatolylformamidine, also prepared by Senier (*loc. cit.*), crystallises from benzene in large, flat, transparent, colourless prisms, and melts at 140°.

The sodium formotoluidides may be converted into the corresponding methyltoluidines by treatment with methyl iodide and sodium methoxide in the presence of dry methyl alcohol, or after Hepp's method for the preparation of methylaniline (*Ber.*, **10**, 328).

Other formanilide derivatives have also been prepared. *Ethylisoformanilide*, NPh:CH·OEt, is an oil boiling at 213—215° under 761 mm. pressure, and having an aromatic odour. *Propylisoformanilide* boils at 233—235° under 760 mm. pressure. *Phenylbenzylformamidine* is formed when a mixture of benzylamine (1 mol.) and methylisoanilide (1 mol.) is kept for some time; the solid product is pressed free from oil, dissolved in alcohol, and reprecipitated, eventually in crystalline form, by water. It forms colourless, transparent, flat prisms, and melts at 80°. *Phenylhydroxyformamidine*, OH·NH·CH:NPh, is obtained as a white solid by adding methyl isoformanilide to an aqueous alcoholic solution of hydroxylamine hydrochloride. When purified by solution in alcohol and reprecipitation with ammonia, it crystallises in small, white needles, and melts at 130—131°. When dry silver formorthotoluidide is distilled, diorthotolylcarbamide (m. p. 247°) is formed. Jn. W.

Acetoacetanilide. By L. Knorr (*Ber.*, **25**, 775—778).—*β-Amidocrotonanilide*, $NH_2\cdot CMe{:}CH\cdot CONHPh$, is prepared by treatment of acetoacetanilide in concentrated alcoholic solution with ammonia; it crystallises from dilute alcohol, and melts at 145°. The methylamido-derivative has been previously described (compare preceding abstract). *β-Dimethylamidocrotonanilide*, $NMe_2\cdot CMe{:}CH\cdot CO\cdot NHPh$, is obtained in a similar manner to the amido-compound, and crystallises from alcohol in small needles melting at 160°.

Acetoacetanilide also yields a phenylhydrazone melting at 108·5°, and an oxime melting at 115°, which will be described later; with hydrazine hydrate, methylpyrazolone (m. p. 215°) is formed.

The preceding amido-compounds are very unstable, and are resolved into their components by boiling with water, or by the action of acids; it was therefore impossible to determine their constitution; the formulæ given are derived by analogy from the dimethylamido-derivative. J. B. T.

β-Methylamidocrotonanilide. By L. Knorr and H. Tauffkirch (*Ber.*, **25**, 768—775; compare Brühl, this vol., p. 730).—

Brühl's "antipyrine alcohol" appears to be *β-methylamidocrotonanilide*, NHMe·CMe:CH·CO·NHPh, since a compound identical with the alcohol is formed by the action of methylamine on acetoacetanilide in concentrated alcoholic solution. On hydrolysis, the compound is resolved quantitatively into its constituents, whilst antipyrine alcohol would probably yield symmetrical methylphenylhydrazine. The production of β-methylamidocrotonanilide by the reduction of antipyrine affords an additional proof of the correctness of Knorr's formula, $NPh<\begin{matrix}NMe\cdot CMe\\ CO—CH\end{matrix}$, for the latter compound, and is analogous to the decomposition of phenylpyrazole by the action of sodium in alcoholic solution.

The authors suggest that the compound supposed by Brühl to be a sodium salt of antipyrine alcohol is really a complicated carbamate, COONa·NPh·CO·CH:CMe·NMe·COONa, which is decomposed by water into sodium carbonate and methylamidocrotonanilide.

J. B. T.

Colour Reaction of Acid Anilides. By J. Tafel (*Ber.*, **25**, 412—413).—When simple anilides, or phenylcarbamides, are dissolved in concentrated sulphuric acid and treated with potassium dichromate, lead dioxide, or ferric chloride, they give a colour resembling that exhibited by strychnine under similar circumstances. Such colours are also produced, according to Bülow (*Annalen*, **236**, 195), in the case of the acid phenylhydrazides, and according to De Neufville and v. Pechmann (Abstr., 1891, 349) in that of phenylhydrazones and phenylosazones. The colours from the anilides are less intense, and more fugitive, than those from the hydrazides and hydrazones, and the latter colours are not produced by ferric chloride. When the substance is dissolved in concentrated sulphuric acid and treated with pulverised potassium dichromate, the anilide and phenylhydrazide of the same acid give a like colour. The products of the action of acetic anhydride or benzoic chloride on ethylaniline and methylaniline, unlike the acetyl and benzoyl derivatives of tetrahydroquinoline, do not exhibit the reaction; further, acetylparatoluidine gives it, whilst acetylorthotoluidine does not. A list is given in the paper, showing the tint produced by several anilides.

A. R. L.

Derivatives of Orthotoluylenediamine. By W. Autenrieth and O. Hinsberg (*Ber.*, **25**, 604—607).—Orthotoluylenediamine is without action on mandelic acid and on benzalacetone, but readily combines with ethyl oxalacetate, forming *ethyl hydroxytoluquinoxalineacetate*, $C_7H_6<\begin{matrix}N:C\cdot OH\\ N:C\cdot CH_2\cdot COOEt\end{matrix}$, which has a yellow colour, melts at 172—173°, and behaves as a phenol. On long-continued boiling with aqueous soda, alcohol and carbonic anhydride are eliminated, hydroxymethyltoluquinoxaline being formed. Thus prepared, the latter melts at 217—218°, whilst, when obtained from pyruvic acid, it melts at 220° (*Annalen*, **237**, 351). As the latter appears to be a

mixture of two isomerides, the compound melting at 172—173° is also probably a mixture of two isomerides, which crystallise together.

When molecular quantities of ethyl chloracetoacetate and orthotoluylenediamine are allowed to remain together in alcoholic solution, a substance separates out in colourless crystals; it is purified by washing with alcohol, and has then the composition $C_{13}H_{17}N_2O_2Cl$, melts at 110°, is insoluble in water, readily soluble in alcohol and ether, and is resolved by acids and alkalis into the compounds from which it is obtained; it has, therefore, probably the constitution $C_7H_6<^{NH}_{NH}>CMe{\cdot}CHCl{\cdot}COOEt$, and is analogous to the compound obtained from orthotoluylenediamine and ethyl acetoacetate. This is confirmed by the fact that the dilute alcoholic solution, when boiled, decomposes into ethenyltoluylenediamine and ethyl chloracetate.

H. G. C.

Mixed (Fatty Aromatic) Azo-compounds. By L. Claisen (*Ber.*, **25**, 746—748).—The sodium derivative of benzeneazoacetylacetone (see Beyer and Claisen; Abstr., 1888, 828) reacts with diazobenzene chloride, forming a diazo-derivative, $CAc_2(N_2Ph)_2$, and a compound having the composition of an acetonedisazobenzene, $C_3H_4O(N_2Ph)_2$, identical with that obtained by the action of diazobenzene chloride on benzeneazoacetoacetaldehyde, and also with the mesoxaldehydebisphenylhydrazone described by Bamberger (this vol., p. 162).

A. R. L.

Action of Hydroxylamine on Paradiazotoluene and Diazobenzene Chlorides. By J. Mai (*Ber.*, **25**, 372—374).—E. Fischer, in 1878, obtained diazoimidobenzene by the action of diazobenzene sulphate on hydroxylamine hydrochloride in aqueous solution. The author finds that when paratoluidine (2 grams) is diazotised in the presence of hydrochloric acid, and to the cooled solution, one of hydroxylamine hydrochloride (3 grams) and potassium hydroxide (4 grams) is added, a mixture of nitrogen and nitrous oxide is evolved; on now acidifying and removing the precipitated oil with ether and adding alkali, paratoluidine separates. In a similar manner diazobenzene chloride yields aniline. He believes that an intermediate product is formed, and is now engaged in studying the reaction between β-methylhydroxylamine and paradiazotoluene chloride, in the hope of obtaining information as to the mechanism of the reaction.

A. R. L.

Acid Hydrazides. By J. Tafel (*Ber.*, **25**, 413—415).—*Acetyldiphenylhydrazine*, $NPh_2{\cdot}NHAc$, is obtained by boiling acetylphenylhydrazine (1 mol.) with copper acetate (2 mols.) in aqueous or alcoholic solution, preferably the latter; the compound is identical with that obtained by boiling diphenylhydrazine with glacial acetic acid; it forms bunches of lustrous needles, melts at 184°, distils undecomposed, and is sparingly soluble in ether and light petroleum, more readily in warm benzene and chloroform. It gives an intense violet colour on heating with dilute sulphuric acid and potassium dichromate, and dissolves in concentrated sulphuric acid with a green

colour, which on warming, or on the addition of an oxidising agent, passes into a beautiful blue; it yields a colouring matter when heated with concentrated hydrochloric acid and alcohol in a sealed tube at 100°.

Benzoyldiphenylhydrazide, identical with that described by E. Fischer (Abstr., 1878, 313), is obtained by boiling benzoylphenylhydrazine with copper acetate in alcoholic solution. A. R. L.

So-called Physically Isomeric Hydroxylamine Derivatives. By W. Lossen (*Ber.*, **25**, 433—442).—Further investigations carried out in the author's laboratory have proved that about 16 hydroxamic acid derivatives, in addition to the nine previously described (Abstr., 1889, 1064), exist in different modifications; Werner (this vol., p. 461) has discovered the existence of two, or perhaps three, new cases of the same kind. All the derivatives referred to, which have been prepared by the author and his pupils, are ethereal salts of hydroxamic acids, or alkylhydroxamic acids, or triacidyl derivatives of hydroxylamine; Werner has shown that ethereal salts of alkylhydroxamic acids also exist in different modifications.

Only three hydroxamic acid derivatives are known to exist in three different modifications, namely, tribenzhydroxylamine, benzanisobenzhydroxylamine, and ethyl paratolylbenzhydroxamate. The conversion of one modification into the other has been accomplished only in isolated cases; it has also been proved that, in the case of many hydroxamic acid derivatives, the different modifications have the same molecular weight, also that they differ from one another in chemical behaviour. A full description of the experiments here mentioned will be published in the *Annalen*.

The rest of the article consists of a severe criticism of some of Werner's experiments, and of the system of nomenclature suggested by him. F. S. K.

Action of Nitric Acid on Alkyl Phenylcarbamates. By P. van Romburgh (*Rec. Trav. Chim.*, **10**, 135—144).—Methyl phenylcarbamate prepared according to Hentschel's method (Abstr., 1885, 883) is dissolved in nitric acid (sp. gr. 1·46), and the mixture is poured into water; the yellowish-red product is purified by recrystallisation from alcohol and ether, or a purer yield is obtained by boiling methyl phenylcarbamate with nitric acid, since in the cold some trinitro-derivative is also formed. As thus obtained, the *dinitro*-derivative, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}COOMe$, forms pale-yellow needles; it melts at 127°, dissolves in hot alcohol and ether, and in cold acetone, acetic acid, ethyl acetate, chloroform and benzene, but is only slightly soluble in carbon bisulphide and light petroleum. Neither potassium carbonate nor alcoholic ammonia reacts with this compound, and it is but slightly attacked by hydrochloric acid at 150°. Aqueous potash, after some days contact, converts it into dinitraniline melting at 175°, whence its probable constitution is $[NH : (NO_3)_2 = 1 : 2 : 4]$.

The trinitro-derivative $[NH : (NO_2)_3 = 1 : 2 : 4 : 6]$ is formed by dissolving the dinitro-derivative in nitric acid (sp. gr. 1·5), or by adding a solution of methyl phenylcarbamate in 5 parts of sulphuric acid

to fuming nitric acid. Either of these solutions is poured into water, and the yellow product on recrystallisation from alcohol forms needles or plates which melt at 192°. Hentschel (Abstr., 1887, 143) claims to have similarly obtained a tetranitrodiphenylcarbamide; the author, however, identifies the product with his own methyl trinitrophenylcarbamate. This substance dissolves in the same media as the dinitro-derivative, from which it differs in yielding picramide (m. p. 188°) when left in contact with alcoholic ammonia for some days, and on heating with hydrochloric acid at 150° for some hours, carbonic anhydride, chloroform, and picramide are produced. This trinitro-derivative dissolves in potassium hydroxide solution, and decomposes potassium carbonate forming a crystalline salt, $C_9H_7KN_4O_8$; with silver nitrate, it yields a silver salt, which reacts with methyl iodide to form a crystalline methyl derivative. A yellow, crystalline compound, $C_9H_8N_4O_8 + NHMe_2$, of the trinitro-derivative with dimethylamine has been prepared melting at 138° with decomposition.

From ethyl phenylcarbamate corresponding derivatives are similarly prepared. Ethyl dinitrophenylcarbamate has previously been described by Hager (Abstr., 1885, 149). It crystallises from boiling alcohol in clear, yellow needles, melts at 110°, and affords the same dinitraniline as the methyl derivative when left in contact with dilute aqueous potash.

Ethyl trinitrophenylcarbamate forms yellowish-white plates, melts at 144°, is somewhat more soluble than the methyl derivative, but yields the same decomposition products, as also a compound with dimethylamine, and a silver salt which reacts easily with methyl iodide. T. G. N.

Diparatoluamide and Diorthotoluamide. By F. Krafft and H. Karstens (*Ber.*, **25**, 452—460; compare Abstr., 1890, 1289). —*Imidodiparatoluamide*, $C_6H_4Me{\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}C_6H_4Me$, is precipitated in colourless needles when paratolunitrile is treated with anhydrosulphuric acid in the cold, the product extracted with a large quantity of cold water, and the filtered aqueous extract treated with ammonia; it can be recrystallised from warm alcohol without undergoing any notable decomposition, and then melts at 145°.

Diparatoluamide, $NH(CO{\cdot}C_6H_4Me)_2$, is deposited in lustrous needles when the aqueous extract just referred to is warmed for some time at about 70°; it melts at 155°, and on distillation, even under greatly reduced pressure, it is decomposed into paratolunitrile and paratoluic acid. It is only slowly decomposed by boiling water and very dilute acids, but when heated with water at about 140°, it is quickly converted into paratoluic acid and paratoluamide.

Imidodiorthotoluamide can be obtained by warming orthotolunitrile with anhydrosulphuric acid for some time at 60—70°, then extracting the product with a little cold water, and adding ammonia to the filtered extract; it crystallises from warm alcohol in small, lustrous prisms melting at 103°.

Diorthotoluamide is formed when the aqueous extract just mentioned is heated at 60—70° for some time; it separates from warm alcohol in slender crystals, and melts at 147—148°. It is decomposed

into orthotolunitrile and orthotoluic acid on distillation, but when heated with water, it gives orthotoluic acid and orthotoluamide.

The constitution of the diamides may, according to the present views, be formulated in two ways; the constitution of dibenzamide, for example, may be expressed by the formulæ $NHBz_2$ and NH:CPh·OBz, so that the existence of two phenyl derivatives of dibenzamide is, theoretically, possible. As a matter of fact, two such compounds have been described: the one, $NPhBz_2$, prepared by Gerhardt and Chiozza by heating benzanilide with benzoic chloride, melts at 136°; the other, obtained by Losanitsch by heating phenylthiocarbimide with benzoic acid, melts at 155°. The authors find, contrary to the results obtained by Higgin (Trans., 1882, 133), that Losanitsch's compound is simply benzanilide (m. p. 160—161°), this substance being readily formed, together with carbon oxysulphide, by the interaction of benzoic acid and phenylthiocarbimide in molecular proportion at 130°; a similar reaction takes place when acetic acid is heated with phenylthiocarbimide, acetanilide and carbon oxysulphide being produced. As, therefore, the existence of two isomeric alkyl derivatives of dibenzamide is not yet proved, the symmetrical formula given above should be employed, at any rate provisionally, to represent the constitution of dibenzamide.

F. S. K.

Action of Sulphuric Anhydride on Nitriles. By P. Eitner (*Ber.*, **25**, 461—472; compare preceding abstract).—A neutral additive compound of the composition $(C_6H_5{\cdot}CN)_2SO_3$ is deposited in yellow crystals when well-cooled benzonitrile is treated with the vapour of sulphuric anhydride. It crystallises from warm benzene in colourless, seemingly monoclinic prisms, begins to decompose at 120° with formation of benzonitrile, melts at 157—158°, and sublimes under reduced pressure with only slight decomposition; it is readily soluble in benzene, toluene, xylene, and chloroform, but only very sparingly in light petroleum and carbon bisulphide, and insoluble in ether, water, and alkalis. The following experiments show that the constitution of this compound is most probably expressed by the formula $N\leqslant^{CPh:N}_{CPh\cdot O}>SO_2$; it may, therefore, be named *benzoylsulphobenzamidinic anhydride*. When heated with water at about 120°, it is decomposed into benzoic acid and ammonium sulphate; it dissolves in sulphuric acid with development of heat, giving a pale-yellow solution from which, on the addition of water and excess of ammonia successively, imidodibenzamide is precipitated.

Imidodibenzamide (m. p. 105—106°) can be prepared by heating benzenylamidine hydrochloride with benzoic chloride at about 110°; when warmed with dilute sulphuric acid, it is decomposed into ammonia and dibenzamide, and on distillation, even under a pressure of 11 mm., it undergoes decomposition into benzonitrile, benzamide, and small quantities of cyaphenine. The *hydrochloride*, $C_{14}H_{12}N_2O,HCl$, is a colourless, crystalline powder melting at 187—188°. When imidodibenzamide is boiled for a long time with alcohol, it yields ethyl benzoate, benzamide, and cyaphenine with evolution of ammonia.

Sulphobenzamidinic acid, $NH_2 \cdot CPh{:}N \cdot SO_3H$, is formed, together with ethyl benzoate, when benzoylsulphobenzamidinic anhydride is boiled with alcoholic benzene containing a few drops of water; it separates from hot water in prisms, and from cold water in lustrous, monoclinic crystals, and melts at 247°. The *barium* salt,

$$(C_7H_7N_2SO_3)_2Ba + 4H_2O,$$

separates from hot water in large, colourless, transparent, monoclinic crystals, and loses the whole of its water at 140—150°. The *calcium* salt, $(C_7H_7N_2SO_3)_2Ca$, forms anhydrous crystals, and is much more readily soluble in water than the barium salt. When the barium salt is boiled with dilute hydrochloric acid, it is decomposed into barium sulphate and benzenylamidine sulphate. The acid described by Engelhardt (*J. pr. Chem.*, **75**, 363) under the name of sulphobenzamic acid is identical with the sulphobenzamidinic acid described above. F. S. K.

Iodation of Parabromobenzoic Acid: Salts of Parabromometanitrobenzoic Acid. By O. Hough (*Chem. News*, **65**, 64—65).—No iodation of parabromobenzoic acid occurred when it was heated with iodine and mercuric oxide either with or without pressure.

Potassium parabromometanitrobenzoate is anhydrous, and forms long, yellow, prismatic needles, which are soluble to the extent of 33·44 grams in 100 grams of water. The *sodium salt* contains 1 mol. H_2O, and forms needles, of which 100 grams of water dissolve 16·01 grams. The *ammonium salt* crystallises in anhydrous needles, of which 12·22 parts dissolve in 100 of water.

The small, white needles of the *strontium salt* contain $3\frac{1}{2}$ mols. H_2O, those of the *calcium salt* 13 mols. H_2O; of the former, 0·88 part, of the latter, 1·09 part, dissolve in 100 of water. The *zinc salt* forms white needles, 0·70 part dissolving in 100 of water; a *basic zinc salt* is obtained in minute, yellow plates by precipitating a solution of the potassium salt with zinc chloride.

The *mercury salt* is white and anhydrous, and 0·96 gram dissolves in 100 of water. The *nickel salt* forms pale-green crystals containing $2\frac{1}{2}$ mols. H_2O; 1·47 parts of this, and 1·05 parts of the *cobalt salt*, dissolve in 100 of water. The latter salt forms pink needles with 3 mols. H_2O. All solubilities are for a temperature of 26°.

D. A. L.

Hydrobenzoic Acids. By V. Markovnikoff (*Ber.*, **25**, 370—371).—The author informed Aschan in a private communication that hexahydrobenzoic acid melts at 28°, whereas the latter made no mention of this information in his paper (Abstr., 1891, 1481). Pure hexahydrobenzoic acid melts at 28·5—29·5°, is heavier than water, and sparingly soluble in it at the ordinary temperature, more readily in the hot liquid; it has a faint odour recalling that of valeric and ethylcrotonic acids, and boils at 232—233° (compare Aschan, *loc. cit.*). It does not combine with bromine, but when dissolved in sodium carbonate solution and treated with potassium permanganate solution (1 part of the salt in 1000 parts of water), it is scarcely possible to distinguish it from the tetrahydro-acid by the rate at which the per-

manganate is decolorised. Its composition was placed beyond doubt by complete analysis of the silver salt. The crude hydrogenation product contains also a crystalline acid of very low melting point and a liquid acid, both of which combine with bromine and decolorise permanganate; an acid boiling above 260° is also present in small quantity, and valeric acid, evidently produced by the protracted boiling of the sodium amyloxide, is obtained from the lower fractions. A. R. L.

Methyl Mesitylenecarboxylate. By E. Feith (*Ber.*, **25**, 503).—Methyl mesitylenecarboxylate is an oil which boils at 242—244°. The author has erroneously described this compound as crystallising in plates and melting at 139—140° (this vol., p. 329). E. C. R.

Dichlorhydrin Parahydroxybenzoate. By C. Götting (*Ber.*, **25**, 811—813).—By the action of hydrogen chloride on parahydroxybenzoic acid and glycerol at 100°, and treatment of the product with water, a viscid liquid is obtained which solidifies after some time; it is formed in larger quantity at 70—75°. The compound is readily soluble in alcohol, ether, and benzene, crystallises in colourless, radial, feathery aggregates, and melts at 74—76°; on hydrolysis with alkalis, it yields epichlorhydrin together with impure hydroxybenzoic acid; and, from the fact that it is most readily formed at temperatures below 100°, it appears to be *β-dichlorhydrin parahydroxybenzoate*, $OH\cdot C_6H_4\cdot COO\cdot CH_2\cdot CHCl\cdot CH_2Cl$. J. B. T.

Orthohydroxymethylbenzoic Acid. By E. Hjelt (*Ber.*, **25**, 524—525).—Orthohydroxymethylbenzoic acid, $OH\cdot CH_2\cdot C_6H_4\cdot COOH$, is conveniently prepared by heating phthalide with potash or soda, and acidifying the solution with hydrochloric acid; the precipitated acid is quickly filtered and washed with water; it forms aggregates of lustrous, slender needles melting at 120°, and is stable when anhydrous, but in aqueous solution at ordinary temperatures phthalide is regenerated; the same change is produced more rapidly by the action of acetic chloride on the acid; 100 parts of water at 20° dissolve 0·428 part of the acid; the electrical conductivity $k = 0{\cdot}0151$, $\mu\infty = 353$. The *barium salt* is amorphous; the *potassium salt* crystallises in stellate clusters of needles; it is soluble in alcohol, and yields phthalide on treatment with ethyl iodide. J. B. T.

Derivatives of Gallic Acid and of Pyrogallol. By H. Schiffer (*Ber.*, **25**, 721—727).—*Dibromotriethylgallic acid*, $C_6Br_2(OEt)_3\cdot COOH$, is obtained by brominating triethylgallic acid dissolved in boiling carbon bisulphide; it crystallises from benzene in transparent prisms, melts at 107°, is readily soluble in boiling alcohol and benzene, sparingly in the cold liquids, and dissolves without decomposition in hot concentrated alkalis; it is not attacked by silver oxide, but undergoes complete decomposition when fused with potassium hydroxide. When gallic acid is treated with nitric acid, it yields oxalic acid; whereas the triethyl derivative, when dissolved in glacial acetic acid

and treated with nitric acid (sp. gr. 1·48), gives *nitrotriethylpyrogallol*, $[(OEt)_3 : NO_2 = 1 : 2 : 3 : 5]$; this crystallises in yellowish, silky needles, melts at 74°, and is insoluble in alkalis. The dinitrotriethylpyrogallol described by Benedikt and Weselsky (*Monatsh.*, **2**, 217) is in reality identical with the last-described mononitro-derivative. The latter, when dropped into nitric acid (sp. gr. 1·48), yields a *dinitro*-derivative $[(OEt)_3 : (NO_2)_2 = 1 : 2 : 3 : 4 : 5]$, which is identical with Benedikt and Weselsky's supposed trinitro-derivative (*loc. cit.*); it crystallises from alcohol in small, white needles, and melts at 93°. *Amidotriethylpyrogallol* $[(OEt)_3 : NH_2 = 1 : 2 : 3 : 5]$, prepared by reducing the mononitro-compound with tin and hydrochloric acid, crystallises in small, white needles, melts at 104°, and is readily soluble in alcohol and ether, but only sparingly in hot water; the hydrochloride, platinochloride, and sulphate are crystalline. When the amido-derivative is dissolved in strong sulphuric acid and treated with potassium nitrite, the hydroxy-derivative (hydroxytriethoxybenzene) is obtained; this crystallises in small needles, melts at 105°, and is readily soluble in alcohol and ether, sparingly in boiling water, and is not decomposed by alkalis. Will has shown (Abstr., 1888, 458) that trimethylpyrogallol, when treated with nitric acid, yields a nitro-derivative, together with dimethoxyquinone; this the author confirms, but he finds that triethylpyrogallol, on treatment with nitric acid, yields only a nitro-derivative. Schlör obtained asymmetrical tetrahydroxybenzene from the dimethoxyquinone, and the same compound appears to be formed when the above-mentioned hydroxytriethoxybenzene is treated with hydriodic acid.

Nitrotriethylgallic acid $[(OEt)_3 : NO_2 : COOH = 1 : 2 : 3 : 4 : 5]$ obtained by nitrating triethylgallic acid dissolved in glacial acetic acid, crystallises in delicate yellow needles, melts at 104°, and is readily soluble in alcohol and ether, but only sparingly in hot water; when added to moderately concentrated, cooled sulphuric acid, dinitrotriethylpyrogallol (m. p. 93°) is formed, but it remains unaltered when heated at 200° with dilute acid.

Amidotriethylgallic acid is prepared by boiling a solution of the last-described nitro-derivative in aqueous alcohol with tin and hydrochloric acid; it is easily soluble in alkalis and acids, alcohol, and ether, but only sparingly in cold water; it melts at 111°, and appears to yield an amidotriethylpyrogallol when heated.

Trimethylgallic acid, when nitrated in glacial acetic acid solution, yields a nitrotrimethylpyrogallol identical with that prepared by Will and by Schlör, which has the constitution $[(OMe)_3 : NO_2 = 1 : 2 : 3 : 5]$; so that it would seem that, when the alkyl derivatives of gallic acid are nitrated, the carboxyl group is first displaced, and the constitutions given for the compounds described in this paper are therefore established. A. R. L.

Chestnut-wood Tannin. By H. Trimble (*Proc. Chem. Sect. Franklin Inst.*, **3**, 80—83).—The tannin was obtained from the wood of the *Castanea vesca* of Linnæus, or *C. sativa* of Miller, variety *Americana*. The finely powdered wood was percolated with commercial ether, the ether evaporated, and the residue dissolved in cold

water. The filtered solution was precipitated in three portions by lead hydroxyacetate, the precipitate decomposed by hydrogen sulphide, and excess of the latter removed by distillation under reduced pressure. The residual solution was cooled, agitated with ether to extract gallic acid, and then saturated with salt. The tannin separated out and was washed with a saturated solution of common salt, dried, dissolved in ether-alcohol, and the filtered solution evaporated under diminished pressure. The tannin was thus obtained as a porous, light-red mass. It was further purified by a repetition of the above treatment, and was then obtained as a white, porous mass completely soluble in cold water. It appears to be gallotannic acid, for it resembles this substance in all its reactions, and the results of analysis agree moderately well with this view of its composition, after allowance has been made for 8 per cent. of glucose which exists in it, no doubt as a glucoside. When heated to 200°, it decomposes into pyrogallol and metagallic acid. C. F. B.

ε-Chloramylamine and Synthesis of Piperidine. By S. Gabriel (*Ber.*, **25**, 415—422).—*γ-Chloropropyl phenyl ether*,

$$OPh\cdot CH_2\cdot CH_2\cdot CH_2Cl,$$

can be obtained by warming trimethylene chlorobromide with sodium phenoxide in alcoholic solution; it is a colourless oil boiling at 238—240° under a pressure of 745 mm.

Phenoxypropylmalonic acid, $OPh\cdot[CH_2]_3\cdot CH(COOH)_2$, is formed when the preceding compound is boiled with an alcoholic solution of ethyl sodiomalonate, and the oily product hydrolysed with alcoholic potash. It crystallises from hot water, in which it is readily soluble, in flat, colourless plates, sinters together at 70°, and melts at 75—80° to a turbid liquid which does not become quite clear until the temperature has risen to 90—95°, evolution of carbonic anhydride then taking place.

δ-Phenoxyvaleric acid, $OPh\cdot[CH_2]_4\cdot COOH$, prepared by heating the dicarboxylic acid above its melting point, separates from light petroleum in compact, transparent crystals, melts at 65—66°, and boils at 315—320° with partial decomposition; it is readily soluble in alcohol and light petroleum. The *silver* salt, $C_{11}H_{13}O_3Ag$, crystallises in microscopic needles.

δ-Phenoxyvaleronitrile, $OPh\cdot[CH_2]_4\cdot CN$, is obtained when the corresponding acid is heated with lead thiocyanate; it is a colourless, crystalline compound, melts at 28—30°, and boils at 299—304°, seemingly with slight decomposition.

ε-Phenoxyamylamine, $OPh\cdot[CH_2]_5\cdot NH_2$, prepared by reducing the nitrile with sodium and alcohol, is a colourless oil which boils at 274—275°, and solidifies at a low temperature to a mass of crystals; it is only sparingly soluble in water, to which it imparts an alkaline reaction, and it absorbs carbonic anhydride, forming a crystalline carbonate. The *hydrochloride*, $C_{11}H_{17}NO,HCl$, crystallises from dilute hydrochloric acid in compact needles, and melts at 138—140°. The *platinochloride* is a yellow, crystalline, sparingly soluble compound, which sinters together at about 200°, and melts at about 210°. The

picrate separates from hot alcohol in small, rhombic crystals, melts at 147—148°, and is only sparingly soluble in cold water.

ε-Chloramylamine hydrochloride, $CH_2Cl\cdot[CH_2]_4\cdot NH_2,HCl$, is formed when phenoxyamylamine is heated at 180° with concentrated hydrochloric acid. It crystallises from a mixture of alcohol and ethyl acetate in yellowish scales, sinters together at 140°, melts completely at 152°, and is very readily soluble in water. The *picrate*, $C_5H_{12}NCl,C_6H_3N_3O_7$, crystallises in flat, yellow needles, and melts at 123—125°. The *platinochloride*, $(C_5H_{12}NCl)_2,H_2PtCl_6$, crystallises from warm water in lemon-yellow plates, and melts at 95—97° with previous softening. When the hydrochloride (1 mol.) is warmed with dilute soda (1 mol.), it is converted into piperidine hydrochloride. F. S. K.

Nitration of Butyltoluenesulphonic Acid and of Butylxylenesulphonic Acid. By E. Noelting (*Ber.*, **25**, 785—792).—*Dinitrobutyltoluenesulphonic acid*, $C_4H_9\cdot C_6HMe(NO_2)_2\cdot SO_3H$

$$[= 3:1:2:4:6],$$

is prepared by dissolving the sulphonic acid in 6—8 parts of nitric acid (86 per cent.), and allowing it to remain for a considerable time at the ordinary temperature. The product is treated with water, the solution extracted with ether in order to remove trinitrobutyltoluene, neutralised with baryta and barium carbonate, and evaporated to dryness. The *barium sulphonate* is separated from the inorganic salts by treatment with alcohol; it crystallises from water in colourless plates containing 7 mols. H_2O. The *sodium salt*, with 3 mols. H_2O, crystallises from water in large, colourless plates. The *free acid* is readily soluble in water, and, like the salt, is odourless; its constitution is proved by the fact that on warming with nitric acid it yields symmetrical trinitrobutyltoluene; the butyltoluenesulphonic acid, when fused with potash, yields, according to an unpublished research of Baur, butylcresol, $C_4H_9\cdot C_6H_3Me\cdot OH$ [Me : C_4H_9 : OH = 1 : 3 : 6].

Dinitrobutylmetaxylenesulphonic acid, $C_4H_9\cdot C_6Me_2(NO_2)_2\cdot SO_3H$, is prepared in a manner similar to the toluene derivative, which it closely resembles; the *barium salt* is readily soluble in water; the *sodium salt* crystallises in silvery, lustrous plates, and is extremely soluble in alcohol.

By the interaction of metaxylene, isobutyl alcohol, and sulphuric acid at 45°, tertiary butylmetaxylene is formed; it readily yields a sulphonic acid, the *anilide* of which crystallises from dilute alcohol in colourless needles melting at 143·5—144·5°. Tertiary butylmetaxylene is also obtained by the action of zinc chloride on metaxylene and isobutyl alcohol. Trinitrobutylmetaxylene smells strongly of musk, but the dinitrosulphonic acid and its salts are odourless. J. B. T.

Substitution Products of Stilbene and Thionessal. By K. Kopp (*Ber.*, **25**, 600—603).—By the distillation of polymerised thiobenzaldehyde, Laurent obtained a mixture of stilbene and a substance termed thionessal, which has been proved by Baumann and Klett to be tetraphenylthiophen (this vol., p. 184). The author has investi-

gated the action of heat on other polymerised thioaldehydes, in the hope of obtaining stereoisomeric stilbenes, but hitherto no indication of their formation has been observed. In the present paper, the results obtained with the methoxythiobenzaldehydes are described.

When polymerised methylthiosalicylaldehyde (Abstr., 1891, 1050) is heated for five hours at 145°, a transparent, reddish mass is formed which, by repeated crystallisation from ether, may be obtained in colourless prisms having a blue fluorescence. It consists of *diorthomethoxystilbene*, $C_2H_2(C_6H_4{\cdot}OMe)_2$, melts at 136°, is readily soluble in alcohol, chloroform, and benzene, and insoluble in water. No second isomeride could be obtained from the mother liquors, but the yield is greatly affected by the formation of the substituted thionessal, which takes place almost completely at temperatures above 150°. A better yield of the stilbene derivative is obtained by distilling the aldehyde with iron powder, a small quantity of an unpleasant smelling oil being the only other product; if zinc-dust is employed instead of iron, considerable quantities of the thionessal are formed. To prepare the latter, the mass obtained by heating the aldehyde to temperatures above 150° is powdered, freed from colouring matter by trituration with alcohol, and recrystallised from alcohol or acetic acid. It forms woolly needles, melts at 136°, and has the composition required by the formula $C_4S(C_6H_4{\cdot}OMe)_4$; in its behaviour towards solvents, it is very similar to diorthomethoxystilbene, but dissolves somewhat less readily in hot acetic acid.

When polymerised thioanisaldehyde is heated, sulphur is not eliminated in any quantity until the temperature has reached 160—170°, the reaction being then complete in three hours. The product, after recrystallisation from benzene, consists of *diparamethoxystilbene*, and forms white, lustrous plates which do not show any fluorescence; it melts at 211°, and is only appreciably soluble in boiling chloroform and benzene. No thionessal derivative appears to be formed on heating this thioaldehyde, even at temperatures far above 200°. H. G. C.

Action of Benzene on Benzal Chloride in presence of Aluminium Chloride. By C. E. Linebarger (*Amer. Chem. J.*, **13**, 556—559).—Triphenylmethane and diphenylanthracene dihydride are the principal products of the reaction.

Aluminium chloride (25 grams) is added to a mixture of benzal chloride (200 grams) and benzene (1000 grams), and the whole is heated at about 50° until a little less than the theoretical amount of hydrogen chloride has been given off (two hours). The reaction is then completed by boiling for a few minutes, and the product is washed with water and fractionated. The fraction passing over between 300° and 360° is chiefly triphenylmethane, and is purified by successive recrystallisation from benzene and alcohol. As thus prepared, it melts at 93·4°, and boils at 357° under a pressure of 758 mm. As the yield is about 30 per cent. of the benzal chloride used, and only traces of diphenylmethane are formed if the materials are pure, this forms an excellent, cheap, and expeditious mode of preparing triphenylmethane.

The fractions boiling above 400° are refractionated under a pressure of 25 mm. More triphenylmethane first passes over, but the fraction distilling above 300° contains *diphenylanthracene dihydride*,

$$C_6H_4<\begin{matrix}CHPh\\CHPh\end{matrix}>C_6H_4,$$

which, on recrystallisation from boiling benzene, is obtained in white, microscopic, rhombic prisms. It melts at 164·2°, boils at 437°, dissolves in alcohol, ether, toluene, and xylene, but is insoluble in water. The yield is 1 per cent. of the benzal chloride used. On bromination in boiling chloroform solution, it yields a dibromide. *Diphenylanthracene dibromide*, $C_6H_4<\begin{matrix}CBrPh\\CBrPh\end{matrix}>C_6H_4$, crystallises in small tablets, melts at 127° with slight decomposition, and dissolves in alcohol, benzene, chloroform, and toluene. Jn. W.

Action of Bleaching Powder and of Hypochlorous Acid on Quinones and Diketones. By T. Zincke (*Ber.*, **25**, 399—410).—The lactone of dihydroxyorthocarboxyphenylpropionic acid,

$$CO<\begin{matrix}C_6H_4\\O\text{—}\end{matrix}>CH\cdot CH(OH)\cdot COOH,$$

is obtained when β-naphthaquinone (3 grams), mixed into a paste with water, is treated with a concentrated solution of bleaching powder (80—90 c.c.). It crystallises in tables or in leaflets resembling phthalic acid, is sparingly soluble in benzene, chloroform, and ether, readily so in hot alcohol or glacial acetic acid, and melts at 202°. It neutralises one equivalent of alkali hydroxide in the cold, but two at a higher temperature, giving rise to salts of the above-mentioned bibasic acid. The *methyl* salt, prepared from the *silver* salt, forms rhombic tables, and melts at 131°, whilst the *acetyl derivative*, $CO<\begin{matrix}C_6H_4\\O\text{—}\end{matrix}>CH\cdot CH(OAc)\cdot COOH$, crystallises in long, lustrous needles, melts at 187°, and yields a *methyl* salt melting at 108°. When the lactonic acid is heated with concentrated hydriodic acid and phosphorus at 150—160°, orthocarboxyhydrocinnamic acid, melting at 163—164° (Gabriel and Michael, Abstr., 1878, 427; Wislicenus, *Annalen*, **242**, 27), is produced.

Dihydroxynaphthaquinone, $C_6H_4<\begin{matrix}CO\text{—}CO\\C(OH):C\cdot OH\end{matrix}$ or $C_6H_4<\begin{matrix}CO\cdot C\cdot OH\\CO\cdot C\cdot OH'\end{matrix}$ is formed when β-naphthaquinone is mixed into a paste with water and treated with concentrated bleaching powder solution (25—30 c.c.). It crystallises from toluene in small, delicate, red needles, does not melt at 250°, dissolves readily in acetone, sparingly in cold alcohol, benzene, and chloroform. Alkalis dissolve it, forming a blue solution, which after a time becomes colourless, and it is converted into phthalic acid by an excess of bleaching powder solution. It is identical with isonaphthazarine, described by Bamberger and Kitschelt (this vol., p. 494). A. R. L.

Sulphonic Acid obtained from 1 : 4-Amidonaphthol. By P. Seidel (*Ber.*, **25**, 423—430).—*Amidonaphtholsulphonic acid*,

$$NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H,$$

is formed when 1 : 4-amidonaphthol hydrochloride, prepared from α-naphthol-orange, is triturated with the theoretical quantity of 10 per cent. anhydrosulphuric acid. It crystallises from boiling water, in which it is only very sparingly soluble, in colourless needles, and turns brown when heated above 200°; its freshly prepared solutions in alkalis and alkali carbonates are grass-green, but turn brown on keeping. It reduces ammoniacal silver solutions, gives with diazosulphanilic acid and sodium acetate a reddish-brown coloration on boiling, and is readily oxidised by potassium permanganate in alkaline solution, and also by warm, concentrated nitric acid with formation of phthalic acid. When the dry, finely-divided sulphonic acid is rubbed to a paste with alcohol, and then warmed with nitric acid of sp. gr. 1·3 for a few minutes, or suspended in alcohol and treated with nitrous acid, it is converted into the ammonium salt of a naphthaquinonesulphonic acid of the composition $C_{10}H_{15}O_2 \cdot SO_2 \cdot ONH_4$. This substance is very readily soluble in water, alcohol, and ether, and exists in two crystallographically different forms, namely, in orange plates and in colourless needles, both of which begin to darken when heated at 220°, and melt above 230° with complete decomposition; it is decomposed by concentrated hydrochloric acid with separation of ammonium chloride, and concentrated nitric acid converts it into phthalic acid; when boiled with aniline and alcohol, it yields β-anilidonaphthaquinone anilide, $NHPh \cdot C_{10}H_5 < \begin{matrix} O \\ \| \\ NPh \end{matrix}$ [NPh : NHPh : O = 1 : 3 : 4].

Diazonaphtholsulphonic acid, $N \ll \begin{matrix} N \\ O \end{matrix} > C_{10}H_5 \cdot SO_3H + H_2O$, is formed when nitrous acid is passed into alcohol containing moist, finely-divided amidonaphtholsulphonic acid in suspension; it crystallises in yellow needles, turns green at about 140°, and explodes at 160°. It is moderately easily soluble in cold water, but on the addition of hydrochloric, sulphuric, or nitrous acid to the solution, it is precipitated in large crystals; it loses its water of crystallisation over sulphuric acid, but regains it on exposure to the air. Its alkaline solutions give with phenol, naphthol, &c., deep-red colorations, and with excess of potash an orange, crystalline potassium salt; this salt turns brown when dried at 100°, and then dissolves in alkalis with a purple-red coloration.

A violet oxidation product of the composition $C_{20}H_{14}N_2SO_5$ is formed when an aqueous solution of amidonaphtholsulphonic acid is heated; it crystallises in needles, and is moderately easily soluble in hot alcohol, but only sparingly in hot glacial acetic acid, and almost insoluble in water, benzene, and chloroform. It gives a magenta coloration with concentrated sulphuric acid, but it seems to be unchanged by concentrated hydrochloric acid; when treated with potash, it yields a black oil which, especially after the addition of alcohol, is transformed into bronze crystals of the potassium salt; on reduc-

tion with stannous chloride and hydrochloric acid, it is converted into a colourless substance, which is readily soluble in alcohol, but insoluble in water. Crystals of the oxidation product which have been exposed to an atmosphere saturated with aqueous vapour have the composition $C_{20}H_{14}N_2SO_5 + 5H_2O$, but on keeping over sulphuric acid, they lose approximately 4 mols. H_2O without any alteration in colour or in lustre. F. S. K.

Sulphonic Acids of Amido-α-Naphthol and α-Naphthoquinone. By O. N. Witt (*Ber.*, **25**, 735—736).—The author is engaged on this subject in conjunction with his pupils, and wishes to reserve the same. A. R. L.

Reaction between Triphenylmethane and Chloroform in presence of Aluminium Chloride. By C. E. Linebarger (*Amer. Chem. J.*, **13**, 554—556).—The phenylanthracene which occurs as a secondary product in the preparation of triphenylmethane from chloroform and benzene under the influence of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.* [6], **1**, 495) results from a precisely similar action between the chloroform and the newly-formed triphenylmethane, which may be utilised for the independent preparation of phenylanthracene.

Aluminium chloride (40 grams) is added in three portions to a solution of triphenylmethane (50 grams) in dry chloroform (600 grams), and the mixture is heated until a little less than the theoretical quantity of hydrogen chloride has been given off. The liquid product is washed in succession with cold and boiling water, the chloroform is distilled off, and the residue dissolved in benzene. Resinous matter is now precipitated by the addition of light petroleum, and the residue left on distilling off the solvent is recrystallised from alcohol. Phenylanthracene prepared in this manner crystallises in white tablets, and melts at 152·8°. The maximum yield was 15 per cent.

A small quantity of a hydrocarbon, $C_{20}H_{16}$, melting at 87—88°, and probably phenylanthracene dihydride, was also isolated from the products. Jn. W.

Terpenes. By J. W. Brühl and F. Müller (*Ber.*, **25**, 547—551).—The present communication deals with the composition of oil of laurel; the specimen examined distilled between 175° and 275° under ordinary pressure, and left a viscous residue. The distillate contains lauric acid, but eugenol could not be detected; after treatment with potash and digestion with sodium, a liquid is obtained which boils at 167—171°; it consists of cineole, pinene, and other hydrocarbons; the cineole was identified by means of its bromo- and hydrogen bromide derivatives, the pinene by the preparation of pinene nitrosyl chloride. The fraction boiling at 171° was optically examined; the molecular refraction $\mathfrak{M}_\alpha = 42{\cdot}55$, $\mathfrak{M}_\gamma - \mathfrak{M}_\alpha = 1{\cdot}26$, the sp. gr. at 18°/4° = 0·8785. In addition to the above substances, the crude oil contains large proportions of alcoholic or ketonic compounds, which, like menthol or camphor, combine with sodium, the salts so formed being

decomposed by water. Wallach's conclusion that "laurene" (b. p. 171°) does not exist is thus confirmed, whilst the earlier observations of Gladstone are criticised. J. B. T.

Russian Peppermint Oil and Menthylamine. By G. Andres and A. Andréeff (*Ber.*, **25**, 609—621).—Hitherto investigators have confined their attention to the oxygen compounds contained in peppermint oil, very little being known of the nature of the hydrocarbons it contains. The authors have therefore examined large quantities of Russian oil of peppermint with especial reference to the latter point.

It was found that very little difference exists between the oil prepared from the fresh and from the dried plants, the latter containing, however, as would be expected, rather more of the oxygen compounds. The combined oils were subjected to distillation, and found to boil between 165° and 225°; the residue, on distilling in a current of steam, gave considerable quantities of oil, which, on redistillation, boiled at 207—225°. The menthol was separated from the higher fractions by freezing, and the rest frequently fractioned and treated with metallic sodium. Eventually six fractions boiling at temperatures between 158° and 175° were obtained, and also a fraction boiling at 200—205°, which consists almost entirely of menthone. The fraction 173—175° has the composition of a terpene, and in its physical properties closely resembles lævo-limomene, but its specific rotatory power is $[\alpha]_D = -41{\cdot}09°$ instead of $-105°$. On treatment with the necessary reagents, it yields the dihydrochloride, nitrosochloride, and nitrosoterpene corresponding with lævo-limonene, and must therefore contain this hydrocarbon. The fraction 170—173° has a specific rotatory power of $[\alpha]_D = -30{\cdot}64°$, and also contains lævo-limonene mixed with a larger quantity of another isomeric hydrocarbon. The lower fractions contain a larger percentage of hydrogen, and consist therefore of a mixture of a terpene with a hydrocarbon of the formula $C_{10}H_{18}$, but the authors have been unable to isolate the latter; no indications of the presence of a naphthene of the formula $C_{10}H_{20}$ were observed.

The fraction 200—205° contains chiefly menthone mixed with more or less menthol, and may be converted into the oily oxime. The menthone is a mixture of both optical isomerides, the dextro-derivative being present in the larger quantity, but as the isomerides so readily change one into the other, it is uncertain whether both occur in the original oil.

Menthylamine, which was first prepared by Moriya (Trans., 1881, 77), may, contrary to the statement of Beckmann, be readily obtained by reducing the oxime with sodium in alcoholic solution, some menthone being re-formed at the same time. The latter is removed by acidifying with acetic acid and extracting with ether; the aqueous solution is then partially evaporated, treated with an excess of potash, and the liberated amine taken up with ether. The menthylamine thus obtained boils at 204°, has the sp. gr. 0·8685 at 0°/0°, and the specific rotatory power $[\alpha]_D = -33{\cdot}6°$; it has an odour resembling that of coniine, and rapidly absorbs carbonic anhydride from the air. It yields a white, crystalline *hydrochloride*, and a *platinochloride*,

$(C_{10}H_{19}\cdot NH_2)_2,H_2PtCl_6$, which separates from hot water in golden plates. The menthylamine obtained from dextro-menthoxime has very similar chemical properties; its sp. gr. is 0·8749 at 0°/0°, and its specific rotatory power $[\alpha]_D = -9·26°$, and it is therefore probably a mixture of lævo- and dextro-menthylamine, the first variety consisting of lævo-menthylamine. H. G. C.

The Camphor Group. By G. Oddo (*Gazzetta*, **21**, ii, 505—559).—The author gives an exhaustive summary of our knowledge of camphor and its derivatives. After a criticism of the various constitutional formulæ which have been proposed for camphor by previous authors, he assigns to it the following constitution:—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH_2 \\ | \qquad\quad | \\ CH\cdot CH_2\cdot CH \\ | \qquad\quad | \\ CH_2\cdot CO\cdot CHMe \end{array}$$

W. J. P.

Stereochemistry of the Camphor Group. By G. Oddo (*Gazzetta*, **21**, ii, 560—567).—The author develops the constitutional formula for camphor mentioned in the preceding abstract, and gives spacial formulæ, representing the isomeric camphors, borneols, and camphoric acids. W. J. P.

The Camphor Group. By G. Oddo (*Gazzetta*, **21**, ii, 567—569).—Oppenheim (*Ber.*, 1872, 631) has stated that on oxidising cymene by chromic mixture, a solid substance, having the properties of camphor, is obtained.

The author has repeated this work, taking especial care to purify the cymene employed, but no trace of any substance resembling camphor could be detected. It seems probable, therefore, that the cymene employed by Oppenheim contained traces of terpenes which, on oxidation, yielded isomerides of camphor. W. J. P.

Sapotin: a Glucoside. By G. Michaud (*Amer. Chem. J.*, **13**, 572).—Sapotin exists in the almond-like kernels of the seeds of *Achras sapota*, L., from the dry raspings of which it may be extracted with boiling 90 per cent. alcohol, after the removal of the fat by benzene.

Pure *sapotin*, $C_{29}H_{52}O_{20}$, separates from alcoholic solution in microscopic crystals, which form a white powder, having an acrid, burning taste, and irritating the nose and eyes. It melts with decomposition at 240°, is very soluble in water, easily soluble in boiling alcohol, sparingly soluble in cold alcohol, and insoluble in ether, chloroform, and benzene. It is lævogyrate, the rotatory power in alcoholic solution being $[\alpha]_j = -32·11$. Basic lead acetate produces a gelatinous precipitate in aqueous solutions of sapotin; this is soluble in excess of the reagent, and concentrated sulphuric acid gives a garnet-red colour with the dry substance. It does not react with tannin or alkaline copper tartrate.

Sapotin is hydrolysed by hot dilute sulphuric acid into glucose and

sapotiretin, $C_{17}H_{32}O_{10}$, an amorphous substance, which is very soluble in alcohol, soluble in chloroform, but insoluble in water and ether.

Jn. W.

Preparation of Collidine. By J. Mai and K. Aschoff (*Ber.*, **25**, 374—375; compare Hantzsch, Abstr., 1883, 82).—When a mixture of ethyl collidinedicarboxylate (5 grams) and dry soda-lime (25 grams) is heated in a retort, at first gently and later strongly, collidine passes over, and is rectified, its amount being 70—75 per cent. of the theoretical. When ethyl hydrocollidinedicarboxylate is distilled with soda-lime, ammonia is evolved, and a product having the odour of collidine, consisting apparently of a mixture, is obtained; a homogeneous product is not produced when the last-mentioned ethyl derivative is distilled with sodium ethoxide. A. R. L.

γ-Amidoquinoline. By S. Hoogewerff and W. A. Van Dorp (*Rec. Trav. Chim.*, **10**, 144—147).—Ephraim (Abstr., 1891, 1509) has described an α-amidoquinoline which differs from the author's γ-amidoquinoline, prepared by another method. From a solution of cinchonamide in alkaline potassium hypobromite, acetic acid precipitates a bromamide which melts at 138°. On warming the alkaline solution with aqueous potash, decomposition ensues, and γ-amidoquinoline separates on cooling in hydrated acicular crystals which melt at 70°, or at 90° when dried; when crystallised from hot benzene, the melting point rises to 152—154°. The aqueous solution is alkaline to litmus, and the substance is freely soluble in alcohol, chloroform, hot benzene, and ether, although but slightly soluble in carbon bisulphide and light petroleum. It volatilises slowly in a current of steam and yields crystalline salts with chloroplatinic, picric, and chromic acids. Carbonic anhydride precipitates from the ethereal solution a white, crystalline compound which, melting at 96°, resolidifies and remelts at 150°. The platinochloride, $(C_9NH_6{\cdot}NH_2)_2,H_2PtCl_6 + 2H_2O$, forms fine, salmon-yellow needles which are almost insoluble in water; it melts at 266—270° with decomposition. The dichromate, $(C_9H_8N_2)_2,H_2Cr_2O_7$, forms dark-red, acicular crystals, which are slightly soluble in water. A double silver salt, $(C_9H_8N_2)_2,AgNO_3$, forming long, silky, needles, and combinations with mercuric and cadmium chlorides have been prepared. T. G. N.

Attempted Synthesis of a Nitramine of the Quinoline Group. By J. C. Simon-Thomas (*Rec. Trav. Chim.*, **10**, 148—154).—The author has attempted to make a nitramine of the quinoline series by reactions similar to those employed by Franchmiont and Klobbie (Abstr., 1889, 1143) in obtaining a nitramine from piperylcarbamide.

Tetrahydroquinolylcarbamide, prepared according to Hoffmann and König's directions (Abstr., 1883, 1143), melts at 150·5°, and not at 146·5°, as stated by these authors. This substance, when added to nitric acid at low temperatures, is decomposed with evolution of gas, and no definite crystalline product separates; it is oxidised also even on slightly warming with dilute nitric acid. Advantage is taken of its solubility, without alteration, in concentrated sulphuric acid, and this solution is dropped into a large excess of nitric acid at 0° with

vigorous shaking; no gas is evolved, and on pouring the mixture into water at 0°, yellow flakes separate which, after washing, are crystallised from alcohol. Two products are thus obtained, the more soluble of which is dinitrotetrahydroquinolylcarbamide, the less soluble being dinitrotetrahydroquinoline, resulting from the decomposition of the former substance by dilute nitric acid; it melts at 161°.

Dinitrotetrahydroquinolylcarbamide, $NH_2 \cdot CO \cdot C_9NH_3(NO_2)_2$, forms yellow plates, melts at 191°, dissolves easily in warm acetone, is but slightly soluble in warm water and benzene, and quite insoluble in ether; at its melting point it decomposes, and resolidifies at a much lower temperature. When heated for five hours with barium hydroxide in a reflux apparatus, ammonia is evolved, and from the insoluble residue dinitrotetrahydroquinoline, melting at 161°, is separated, and an almost quantitative yield of this compound is obtained when the carbamide is treated with diluted sulphuric acid (1 in 2) at 100°.

On placing dinitrotetrahydroquinolylcarbamide in nitric acid at 0° and allowing the temperature to rise slowly, equal volumes of nitrous oxide and carbonic anhydride are evolved, but no crystalline compound can be isolated from the liquid.

It thus appears that in the corresponding reactions, tetrahydroquinolylcarbamide differs from piperylcarbamide in the substitution of two nitro-groups for two hydrogen atoms in the benzene nucleus, whereas in the latter substance the substitution occurs in the hydrogen of the carbamide group.

As a dinitro-derivative of methyltetrahydroquinoline exists (Abstr., 1885, 1245), and as tetrahydroquinoline is easily methylated (Abstr., 1883, 1143), the author attempted to prepare the methyl derivative of dinitrotetrahydroquinoline, but was unsuccessful.

Dinitrotetrahydroquinoline is a secondary amine, since it yields a nitrosamine melting at 125—127°, and gives Liebermann's reaction with phenol and sulphuric acid. It does not reduce silver nitrate solution, is not affected by chromic acid mixture, and when heated with nitrobenzene in sealed tubes at 290—300°, a black mass is obtained, whereas by similar treatment, tetrahydroquinoline yields quinoline (Abstr., 1889, 905). T. G. N.

Derivatives of the Methylquinolines and of Metadimethylquinoline. By E. Noelting and E. Trautmann (*Chem. Centr.*, 1891, ii, 942—944; from *Bull. Soc. Ind. Mulhouse*, 1891, 285—324).—The methylquinolines, C_9NH_6Me [Me = 3 and 1 respectively], were prepared by Skraup's method from para- and ortho-toluidine; if the heating was continued long enough, the whole of the toluidine was converted into quinoline. Metadimethylquinoline, $C_9NH_5Me_2$ [Me_2 = 1 : 3], was prepared directly from the acetyl derivative of asymmetrical metaxylidine, which derivative had been made in order to separate this base from the isomeric bases. It is saponified and simultaneously converted into a quinoline derivative, and the reaction is less violent then when the base itself is used. The above-named quinoline derivatives can be more easily nitrated than quinoline itself.

Nitromethylquinoline, $C_9NH_5Me{\cdot}NO_2$ [Me : NO_2 = 3 : 4], is the only product of the nitration of 3-methylquinoline. It melts at 116—117°, and crystallises from alcohol in light-yellow needles, which dissolve very readily in ether, sparingly in hot and scarcely at all in cold water. It is a very feeble base; its salts crystallise well, and are decomposed by water. The *methiodide*, $C_9NH_5Me{\cdot}NO_2$,MeI, crystallises from hot water in nearly colourless rhombohedra, which turn yellow when heated to 100°. *Amidomethylquinoline*, $C_9NH_5Me{\cdot}NH_2$, is obtained by reducing the nitro-compound with iron and acetic acid; it forms pale-yellowish needles melting at 145°, and dissolving very readily in hot water, very sparingly in cold. It yields both mon-acid and di-acid salts. When treated with acetic acid and anhydride, it yields an *acetyl derivative*, $C_9NH_5Me{\cdot}NHAc$, which melts at 160°, and crystallises from hot water in colourless needles. *Hydroxymethylquinoline*, $C_9NH_5Me{\cdot}OH$, is obtained from the amido-compound by the diazo-reaction. It melts at 230°, and forms flat needles which easily turn pink, but become colourless when sublimed. It dissolves in alcohol, but not in cold water, and only very sparingly in hot. It yields well crystallised compounds with bases and acids, and with diazobenzene chloride, it yields an *oxyazo-derivative* which melts at 176°, and crystallises from alcohol in red needles, soluble in alkalis. *Nitroso-oxymethylquinoline* (*methylquinoline quinone oxime*), $NOH{:}C_9NH_4MeO$ [NOH : Me : O = 1 : 3 : 4], is obtained by the action of sodium nitrite on a fairly concentrated hydrochloric acid solution of hydroxymethylquinoline. It decomposes above 200°, crystallises from alcohol in yellow plates, and dissolves sparingly in hot water, benzene, and chloroform, moderately in acetic acid. With iron mordants, it gives a brilliant green colour, which stands washing and is not affected by light. *Nitrohydroxymethylquinoline*,

$$NO_2{\cdot}C_9NH_4Me{\cdot}OH,$$

is obtained by oxidising the oxime with potassium ferricyanide in hot dilute aqueous soda. It decomposes above 200°, crystallises from acetic acid, or alcohol, in brilliant, yellowish-brown plates, and forms salts with acids and alkalis.

Hydroxymethylquinoline, $OH{\cdot}C_9NH_5Me$ [OH : Me = 1 : 2], is obtained by the action of glycerol, strong sulphuric acid, and picric acid on the hydrochloride of amidoorthocresol. It melts at 72—74°, crystallises from dilute alcohol in colourless needles, and volatilises with steam. It gives a green colour with ferrous chloride, and when mixed with copper oxide colours the Bunsen flame green; it will print upon mordanted calico. *Nitroso-oxymethylquinoline* (*methylquinoline quinone oxime*), $C_9NH_4MeO{:}NOH$ [O : Me : NOH = 1 : 2 : 4], is obtained by the action of sodium nitrite on an acetic solution of the hydroxymethylquinoline. It decomposes above 200°, crystallises from alcohol in yellow needles, yields soluble salts with acids and bases, and does not print on mordanted calico. *Nitrohydroxymethylquinoline*, $OH{\cdot}C_9NH_4Me{\cdot}NO_2$, is obtained by oxidising the oxime in alkaline solution with ferricyanide. It melts at 192—193°, is precipitated in yellow needles by the addition of acetic acid to an aqueous solution, and crystallises in red needles from alcohol. It

forms salts with acids and alkalis, and prints a fine yellow with aluminium mordants; with iron mordants, brown.

Hydroxymethylquinoline, $OH{\cdot}C_9NH_5Me$ [OH : Me = 1 : 4], is obtained by heating amidoparacresol with glycerol, sulphuric acid, and picric acid. It melts at 122—124°, crystallises from dilute alcohol in colourless needles, is but little soluble in water, but dissolves in acids and alkalis, yielding yellow solutions; it gives a yellow colour with aluminium mordants. *Nitroso-oxymethylquinoline* (*methylquinoline quinone oxime*), $C_9NH_4MeO{:}NOH$ [O : NOH : Me = 1 : 2 : 4], gives a green colour with iron mordants. *Nitrohydroxymethylquinoline*, $OH{\cdot}C_9NH_4Me{\cdot}NO_2$, obtained from the oxime by means of ferricyanide, melts at 205—206°, crystallises from alcohol in yellow needles, and gives a yellow colour with aluminium and a brown with iron mordants.

Nitromethylquinoline, $C_9NH_5Me{\cdot}NO_2$ [Me : NO_2 = 3 : 4], is obtained from the nitroparatoluidine, $NH_2{\cdot}C_6H_3Me{\cdot}NO_2$ [NH_2 : Me : NO_2 = 6 : 3 : 4], melting at 76° by Skraup's reaction; it melts at 116—117°.

Nitromethylquinoline, $NO_2{\cdot}C_9NH_5Me$ [NO_2 : Me = 1 : 3], is obtained by Skraup's reaction from the nitrotoluidine [NH_2 : NO_2 : Me = 6 : 1 : 3] melting at 114°, using picric acid instead of nitrobenzene. It crystallises from alcohol in yellow needles, and forms no compound with methyl iodide. *Amidomethylquinoline*, $NH_2{\cdot}C_9NH_5Me$, is obtained from the last-mentioned compound by reducing it with alcoholic ammonium sulphide. It melts at 62—64°, forms white needles very soluble in alcohol, and can be sublimed; its *hydrochloride* forms orange-yellow needles very soluble in water. Its *acetyl derivative*, $NHAc{\cdot}C_9NH_5Me$, obtained by the action of acetic acid and anhydride on the preceding compound, melts at 91—92°, crystallises from hot water in plates, dissolves in alcohol, and yields with acids well crystallised colourless salts. Hydroxymethylquinoline, $OH{\cdot}C_9NH_5Me$, obtained from the amido-compound by the diazo-reaction, is identical with that obtained by Fischer and others from methylquinolinesulphonic acid. *Nitroso-oxymethylquinoline* (*methylquinoline quinone oxime*), $C_9NH_4MeO{:}NOH$ [O : Me : NOH = 1 : 3 : 4′ ?], decomposes above 200°, forms very slightly soluble brown plates, and gives no colours with mordants. *Amidochloromethylquinoline*, $NH_2{\cdot}C_9NH_4MeCl$ [NH_2 : Me : Cl = 1 : 3 : ?], is obtained as a bye-product when the nitromethylquinoline is reduced with tin and hydrochloric acid. It melts at 129—130°, crystallises from alcohol in pale-yellow needles, almost insoluble in water, and forms well-crystallised, orange-red mon-acid salts, which are decomposed by water. Its *acetyl derivative*, $NHAc{\cdot}C_9NH_4MeCl$, obtained by the action of acetic acid and anhydride, melts at 136—137°, and crystallises from water or alcohol in white needles.

Nitromethylquinoline, $C_9NH_5Me{\cdot}NO_2$ [Me : NO_2 = 1 : 4], is formed when 1-methylquinoline is treated with nitric acid (sp. gr. 1·39) and strong sulphuric acid. It has been obtained synthetically from nitrotoluidine [Me : NO_2 : NH_2 = 1 : 4 : 6]. It melts at 93°, crystallises from alcohol in yellow needles, and is almost insoluble in cold water. *Amidomethylquinoline*, $C_9NH_5Me{\cdot}NH_2$, is obtained from it by reduction with iron and acetic acid. This substance melts at 143°,

crystallises from water or dilute alcohol in yellow needles, and when heated with glycerol, sulphuric acid, and picric acid, yields *methylphenanthroline*, $C_{12}N_2H_7Me$, which melts at 95—96°, and separates from light petroleum in white crystals. Hydroxymethylquinoline, $C_9NH_5Me{\cdot}OH$, may be prepared from the amido-compound by the diazo-reaction, and is identical with the product obtained by Herzfeld, when orthotoluidinesulphonic acid is converted into a quinoline and fused with an alkali. It melts at 262—263°, and turns black at 240° when slowly heated. It crystallises from alcohol in white needles, and forms with diazobenzene chloride an *oxyazo-derivative* melting at 138—139°, and crystallising from alcohol in red needles, insoluble in water, but soluble in aqueous alkalis. *Nitroso-oxymethylquinoline* (*methylquinoline quinone oxime*),

$$NOH{:}C_9NH_4MeO\ [Me : NOH : O = 1 : 3 : 4],$$

obtained by the action of sodium nitrite on an acetic acid solution of the hydroxymethylquinoline, decomposes above 100°, forms brownish-yellow plates, soluble in alcohol, &c., sparingly soluble in water, and dyes calico, that has been mordanted with iron, green. *Nitrohydroxymethylquinoline*, $NO_2{\cdot}C_9NH_4Me{\cdot}OH$, obtained by oxidising the oxime with ferricyanide in alkaline solution, melts at 181—182°, and crystallises from alcohol in orange needles. *Azomethylquinoline*, $C_9NH_5Me{\cdot}N_2{\cdot}C_9NH_5Me\ [Me : N = 1 : 4]$, is obtained as a bye-product when 4 : 1-nitromethylquinoline is reduced with iron and hydrochloric acid. It melts at 260°, crystallises from acetic acid in orange needles, and is insoluble in hot water and nearly so in alcohol, benzene, and chloroform. *Azoxymethylquinoline*, $\begin{matrix} C_9NH_5Me{\cdot}N \\ | \\ C_9NH_5Me{\cdot}N \end{matrix}\!>\!O$, is obtained as a second bye-product; it melts at 201°, and crystallises from alcohol in small, yellow needles insoluble in water.

Nitrodimethylquinoline, $C_9NH_4Me_2{\cdot}NO_2\ [Me_2 : NO_2 = 1 : 3 : 4]$, is obtained by treating 1 : 3-dimethylquinoline with nitric and sulphuric acids. It melts at 107—108°, and crystallises from alcohol in yellow needles, very slightly soluble in hot water. *Amidodimethylquinoline*, $C_9NH_4Me{\cdot}NH_2$, obtained by reducing the nitro-compound with iron and acetic acid, melts at 91°, crystallises from dilute alcohol in yellow needles, slightly soluble in hot water, and forms red mon-acid and colourless di-acid salts. Treated with acetic acid and anhydride, it yields an *acetyl derivative*, $C_9NH_4Me{\cdot}NHAc$, which melts at 201°, crystallises from hot water in white needles, very soluble in alcohol, and forms colourless salts with acids. *Hydroxydimethylquinoline*, $C_9NH_4Me_2{\cdot}OH$, obtained by adding sodium nitrite to a hydrochloric acid solution of the amido-compound, melts at 197—198°, crystallises from chloroform in white tables, very soluble in alcohol, slightly soluble in benzene and chloroform, and forms salts with acids and bases. C. F. B.

Some Ammonium Compounds. By H. Decker (*Ber.*, **25**, 443—444; compare this vol., p. 630).—When quinoline methyl hydroxide is oxidised with an alkaline solution of potassium ferricyanide, it is converted into 1′-methyl-α-quinolone (m. p. 72°), identical with

the compound prepared by Friedländer and Müller from carbostyril. Quinoline ethiodide behaves in like manner, and yields 1′-ethyl-α-quinolone (m. p. 52°) under the same conditions.

When isoquinoline methiodide is oxidised with an alkaline solution of potassium ferricyanide, it gives 2′-methylisoquinolone, which boils at 325—330° with decomposition; pyridine methiodide and pyridine ethiodide give, under the same conditions, 1-methyl-α-pyridone and 1-ethyl-α-pyridone respectively. Since the methiodides of pyridine, quinoline, isoquinoline, and acridine all show, in this respect, the same behaviour, it follows that the ammonium hydroxides of these bases have all the same structure, their difference in basicity being caused simply by a difference in the carbon nucleus in which the tertiary nitrogen atom is situated. F. S. K.

Pyrogenic Synthesis of Isoquinoline. By A. Pictet and S. Popovici (*Ber.*, **25**, 733—735).—When benzylideneethylamine, prepared according to Zaunschirm's directions (Abstr., 1888, 1077), is slowly distilled through a tube which is filled with pumice, and heated to dull redness, and the dried product fractionated, the fraction passing over between 235° and 240° is found to consist of isoquinoline, which is converted into sulphate, and the latter crystallised from alcohol; it was characterised by several of its derivatives.

A. R. L.

Nitro-derivative of Antipyrine. By E. Jandrier (*Compt. rend.*, **114**, 303—304).—*Nitro-antipyrine* is obtained by dissolving antipyrine in 10 times its weight of monhydrated sulphuric acid, and then adding, drop by drop, nitric acid of sp. gr. 1·35, in quantity equal to about 75 per cent. of the antipyrine. The product is poured slowly into cold water, and the precipitate is crystallised from boiling acetic acid. Nitro-antipyrine forms straw-coloured needles melting at 260°. It is insoluble in cold water, slightly soluble in alcohol, but readily soluble in hot acetic acid. With zinc and acetic acid, or tin and hydrochloric acid, it yields amido-antipyrine, and its diazo-derivative yields a ponceau colouring-matter with β-naphthol. C. H. B.

Alcohol of Antipyrine. By J. W. Brühl (*Ber.*, **25**, 395—397).—The observation that camphor is converted into borneol and camphocarboxylic acid, and menthone into menthol and a dicarboxylic acid, by the simultaneous action of sodium and carbonic anhydride (this vol., p. 201), led the author to examine the behaviour of dimethylphenylpyrazolone (antipyrine), under similar treatment. The *alcohol*, $C_{11}H_{14}N_2O$, is thus prepared:—To a solution of antipyrine (3 mols.) in boiling toluene, through which a current of carbonic anhydride is passing, sodium in the form of wire (4 equivs.) is added; a small quantity of methylamine is evolved, and a yellow precipitate separates; on now adding ice-cold water, the latter dissolves, but reprecipitates in a crystalline form after a time, and is collected; when repeatedly crystallised from dilute alcohol, it forms white prisms, melts at 145°, is sparingly soluble in water, light petroleum, and ether, readily so in other solvents. It combines in

molecular proportion with phenylcarbimide with the formation of the *compound* $C_{18}H_{19}N_3O_3$, melting at 173°, and gives a *benzoyl* derivative melting at 175° with decomposition. When its solutions in water, dilute alcohol, glacial acetic acid, and hydrochloric acid are boiled, it is converted into a compound which crystallises from light petroleum in satiny leaflets, and melts at 86°, whilst methylamine and aniline pass over. (Compare Knorr and Taufkirch, this vol., p. 708.)

A. R. L.

Pyrazole Derivatives. By L. Knorr and P. Duden (*Ber.*, **25**, 759—768).—*Phenylmethylpyrazolidone*, $NPh<^{NH\cdot CHMe}_{CO\cdot CH_2}$, is prepared by heating a mixture of crotonic acid with phenylhydrazine in molecular proportion, first at about 125°, and afterwards for a short time at 160°; the compound crystallises from alcohol in small, colourless needles, and from water in well-developed prisms, melts at 84°, boils at 321° (corr.), is not volatile with steam, and has basic, but not acid, properties, thus differing from the isomeric compound obtained by Lederer from phenylhydrazine and the β-haloïd butyric acid. The yield is 77 per cent. of the theoretical. By the oxidation of the pyrazolidone in alcoholic solution with ferric chloride, the corresponding pyrazolone (m. p. 127°) is obtained, and is identical with the compound formed from ethyl acetoacetate. By the action of ferric chloride in excess in aqueous solution at high temperatures on the pyrazolidone, pyrazole-blue, $NPh<^{N:CMe\quad CMe:N}_{CO\cdot C=\!=C-CO}>NPh$ is produced.

Nitrophenylmethylpyrazolone, $NPh<^{N:CMe}_{CO\cdot CH\cdot NO_2}$, is prepared by dissolving the parazolidone in warm, dilute nitric acid; it is precipitated by the addition of water, and crystallises from alcohol in transparent prisms, and from water in small, colourless needles, which melt at 127° when rapidly heated. By the action of sodium nitrite on the pyrazolidone hydrochloride, nitrosophenylmethylpyrazolone,

$$NPh<^{N:CMe}_{CO\cdot C:NOH},$$

is obtained as a brown, viscid liquid. The dichloropyrazolone, $NPh<^{N:CMe}_{CO\cdot CCl_2}$, is formed from the pyrazolidone by treatment with hydrochloric acid and calcium hypochlorite.

Phenylmethylpyrazole is prepared by the action of bromine or of phosphorus pentasulphide on the pyrazolidone; with bromine in excess, *mono-*, *di-*, and *tri-bromopyrazolones* are formed; the first melts at 128°, and the last at 83°.

On heating the pyrazolone with methyl iodide and methyl alcohol in excess, for 12 hours at 110—140°, *phenyldimethylpyrazolidone* (hydroantipyrine), $NPh<^{NMe\cdot CHMe}_{CO-CH_2}$, is obtained; the product is treated with soda, the alcohol removed, and the base purified by extraction with chloroform and recrystallisation from water; it is

deposited in long, flat needles melting at 107°. The *hydrochloride* crystallises in small, slender, hygroscopic needles; the *picrate* melts at 145—146°. Attempts to convert the base into antipyrine by oxidation were unsuccessful. The difference in behaviour between phenylmethylpyrazolone and phenyldimethylpyrazolidone towards oxidising agents is explained by the formation of a double linking between the carbon and nitrogen atoms, consequent on the removal of two hydrogen atoms in the positions 2 : 3 from phenylmethylpyrazolidone; the removal of hydrogen atoms in the position 3 : 4 would not explain the greater relative stability of the dimethyl compound towards oxidising agents; this affords a further proof of the correctness of Knorr's pyrazolone formula, but tells against the one, $NPh<\begin{matrix}NH\cdot CMe\\ \|\\ CO\cdot CH\end{matrix}$, recently suggested by Nef.

Although the action of phenylhydrazine on crotonic acid differs from its action on cinnamic acid, in so far as no intermediate compounds could be isolated, it is probable that the production of the pyrazolidone is preceded by the formation of a compound

$$NHPh\cdot NH\cdot CHMe\cdot CH_2\cdot COOH.$$

The authors comment on recent papers by Lederer (*Annalen*, **238**, 146) and Claisen (this vol., p. 506), regarding the nomenclature of this class of compounds; Lederer's "hydropyrazolone" and "isopyrazolone" are termed pyrazolidone and 3-pyrazolone respectively. Claisen's suggestion to distinguish the carbon atoms in the pyrazole ring by means of Greek letters is considered to be undesirable, it being simpler to number the whole of the atoms comprising the ring. J. B. T.

Hydroxyquinoxalines and Ethoxyquinoxalines. By W. Autenrieth and O. Hinsburg (*Ber.*, **25**, 492—503).—*Parethoxyquinoxaline*, $OEt\cdot C_6H_3<\begin{matrix}N:CH\\ |\\ N:CH\end{matrix}$, is obtained by adding glyoxal hydrogen sulphite to a hot solution of ethoxyphenylenediamine and precipitating with soda. It is easily soluble in hot water, alcohol, and ether, melts at 81°, is volatile with steam, and has an odour resembling that of aniseed. When reduced with tin and hydrochloric acid, it is partly converted into resinous products, partly split up to form ethoxyphenylenediamine.

Parahydroxyquinoxaline cannot be obtained by hydrolysing the preceding compound with hydrochloric acid. It is easily prepared by adding glyoxal hydrogen sulphite to hydroxyphenylenediamine dissolved in acetic acid. It resembles parahydroxyquinoline in general properties, crystallises from hot water in pale-yellow needles, forms yellow salts both with acids and alkalis, and melts at 245°.

Parethoxydiphenylquinoxaline, $OEt\cdot C_6H_3<\begin{matrix}N:CPh\\ |\\ N:CPh\end{matrix}$, is obtained by boiling a mixture of ethoxyphenylenediamine and dibenzoyl in alcoholic solution for a short time. It crystallises from alcohol in slender, lustrous, pale-yellow needles, melts at 150°, gives a deep-red colora-

tion with concentrated sulphuric acid, and is easily soluble in ether, alcohol, and chloroform, insoluble in water.

Parahydroxydiphenylquinoxaline is obtained by hydrolysing the preceding compound with concentrated hydrochloric acid at 160—180°. It crystallises from alcohol in pale-yellow prisms, melts at 251°, and forms unstable salts both with mineral acids and with alkalis.

Ethoxynaphthazine, $OEt\cdot C_6H_3{:}N_2{:}C_{10}H_6$, is obtained by mixing ice-cold acetic acid solutions of β-naphthaquinone and ethoxyphenylenediamine. It is best purified by cautious sublimation, crystallises from dilute alcohol in slender, yellow needles, is insoluble in water, and melts at 186—187°. Its solution in sulphuric acid is green by reflected light, violet-red by transmitted light. A small quantity of a lower melting isomeride is formed at the same time, but it has not yet been obtained pure.

Parethoxyphenanthrazine, $OEt\cdot C_6H_3<\begin{matrix}N\cdot C-C_6H_4\\ \|\quad\ \ |\\ N\cdot C-C_6H_4\end{matrix}$, is obtained in quantitative proportions by adding an alcoholic solution of the diamine to a hot acetic acid solution of phenanthraquinone. It forms slender, yellowish-white crystals, melts at 210°, is sparingly soluble in ether, alcohol, and acetic acid, more soluble in chloroform, and gives with concentrated sulphuric acid a beautiful, bluish-violet coloration, which, on the addition of water, changes to yellow.

Parahydroxyphenanthrazine is obtained by hydrolysing the preceding compound with hydrochloric acid. It crystallises from acetic acid in slender, sulphur-yellow needles, melts above 300°, sublimes almost unchanged, gives a reddish-violet coloration with concentrated sulphuric acid, and forms salts with sodium hydroxide and hydrochloric acid, which are decomposed by water. It dyes wool and cotton yellow in alkaline baths.

Ethyl ethoxyhydroxyquinoxalineacetate, $OEt\cdot C_6H_3<\begin{matrix}N{:}C\cdot OH\\ |\\ N{:}C\cdot CH_2\cdot COOEt\end{matrix}$, is obtained by gently heating a mixture of ethyl oxalacetate and ethoxyorthophenylenediamine in dilute acetic acid. It crystallises from dilute alcohol in slender, yellow needles, melts at 186°, is almost insoluble in water, easily soluble in alcohol and ether, and gives a colourless solution with sodium hydroxide, and a yellowish-red coloration with concentrated sulphuric acid.

Ethoxyhydroxymethylquinoxaline, $OEt\cdot C_6H_3<\begin{matrix}N{:}C\cdot OH\\ |\\ N{:}CMe\end{matrix}$, is obtained by heating the preceding compound with aqueous sodium hydroxide; it crystallises from dilute alcohol in white leaflets, melts at 224°, and has feeble basic and acid properties.

Parethoxyquinoxalinedicarboxylic acid, $OEt\cdot C_6H_3<\begin{matrix}N{:}C\cdot COOH\\ |\\ N{:}C\cdot COOH\end{matrix}$, is obtained by the condensation of sodium dihydroxytartrate with ethoxyphenylenediamine. It melts at 186° with evolution of carbonic anhydride, is easily soluble in hot water and alcohol, more sparingly so in ether, and gives a deep-red coloration with concentrated sulphuric acid.

Parethoxydihydroxyquinoxaline is obtained by heating metethoxyorthophenylenediamine oxalate at 150—160°; it crystallises in slender, colourless needles, melts above 300°, and is somewhat easily soluble in hot water and alcohol.

Trihydroxyquinoxaline, $OH\cdot C_6H_3<\begin{matrix}N:C\cdot OH\\ |\\ N:C\cdot OH\end{matrix}$, is obtained by heating the preceding compound with concentrated hydrochloric acid at 180°. It forms microscopic needles, is sparingly soluble in the usual solvents, sublimes with partial decomposition, and gives a yellowish-green coloration with concentrated sulphuric acid.

Parethoxypiazthiole, $OEt\cdot C_6H_3\cdot N_2S$, is obtained by heating ethoxyphenylenediamine with sodium hydrogen sulphite at 180° and distilling the product with steam. It crystallises from alcohol in colourless needles, melts at 76—77°, has an intense odour resembling anise seed, and is easily soluble in alcohol and ether, sparingly so in cold water. It yields yellow salts with concentrated mineral acids which are decomposed by water. When boiled with tin and hydrochloric acid, it is converted into hydrogen sulphide and ethoxyphenylenediamine.

Parahydroxypiazthiole is obtained by heating the preceding compound with concentrated hydrochloric acid at 170°; it crystallises in leaflets, is easily soluble in alcohol and ether, and melts at 157—158°.

E. C. R.

Synthesis of Phenotriazines. By M. Busch (*Ber.*, **25**, 445—452).—*β-Phenophenyldihydrotriazine*, $C_6H_4<\begin{matrix}N=N\\ |\\ CH_2\cdot NPh\end{matrix}$, can be obtained by gradually adding an aqueous solution of the theoretical quantity of sodium nitrite to a well-cooled solution of orthamidobenzylphenylhydrazine in a slight excess of dilute hydrochloric acid; it is, however, best prepared from orthamidobenzylaniline (m. p. 86—87°) in a similar manner. It crystallises from dilute alcohol in lustrous, almost colourless plates, melts at 128° with decomposition, and is readily soluble in alcohol, ether, and benzene, but more sparingly in light petroleum, and almost insoluble in water; its salts with mineral acids are only stable in acid solution. The *hydrochloride* crystallises in slender, yellowish-green needles; the *sulphate* is also yellowish-green. The *platinochloride*, $(C_{13}H_{11}N_3)_2,H_2PtCl_6$, crystallises in dark-yellow needles which melt and explode at 130°. The *picrate*, $C_{13}H_{11}N_3,C_6H_3N_3O_7$, crystallises in orange-red needles and melts at 111°, exploding at the same time.

Orthamidobenzylparatoluidine hydrochloride, $C_{14}H_{17}N_2,2HCl$, crystallises from dilute hydrochloric acid in long, compact, seemingly rhombic prisms, and is readily soluble in cold water; the free base has been previously described by Söderbaum and Widman (Abstr., 1890, 1258).

β-Phenoparatolyldihydrotriazine, $C_6H_4<\begin{matrix}N:N\\ CH_2\end{matrix}>N\cdot C_6H_4Me$, prepared by treating orthamidobenzylparatoluidine hydrochloride with nitrous acid under the conditions already described, crystallises from alcohol in lustrous, yellow plates, melts at 151° with decomposition, and is

only sparingly soluble in ether and cold alcohol, but more readily in hot alcohol and benzene; it is very sparingly soluble in light petroleum, and almost insoluble in water. Its salts with mineral acids are only stable in acid solution. The *hydrochloride* crystallises in slender, yellow needles, and is readily soluble in alcohol. The *platinochloride*, $(C_{14}H_{13}N_3)_2,H_2PtCl_6$, crystallises in lustrous, orange needles, begins to turn brown at 148°, and melts at 190° with decomposition and previous softening. The *picrate*, $C_{14}H_{13}N_3,C_6H_3N_3O_7$, crystallises in dark-yellow, lustrous needles, melts and explodes at 132°, and is only sparingly soluble in alcohol. F. S. K.

Triazole. By J. A. Bladin (*Ber.*, **25**, 741—745).—*Nitrophenyltriazolecarboxylic acid*, $CH\ll^{N\cdot N\cdot C_6H_4\cdot NO_2}_{N:C\cdot COOH}$, is prepared by boiling phenyltriazolecarboxylic acid with a mixture of nitric acid (10 parts) and sulphuric acid (5 parts) for 8—10 minutes, pouring into water at 0°, and crystallising the precipitated compound from glacial acetic acid, from which it crystallises in colourless leaflets containing 1·5 mols. of acetic acid, which are given off at 100°; it melts at 202°.

Amidophenyltriazolecarboxylic acid, $CH\ll^{N\cdot N\cdot C_6H_4\cdot NH_2}_{N:C\cdot COOH}$, obtained by reducing the nitro-compound, is a white, crystalline powder which dissolves readily in ammonia, the solution becoming coloured on boiling; it is also soluble in boiling hydrochloric acid, and melts at 212°.

Triazolecarboxylic acid, $CH\ll^{N\cdot N}_{N:C\cdot COOH}$, is produced when the last-described amido-acid (8 grams) is dissolved in 50 per cent. sodium hydroxide (60 grams), and to the warm solution a concentrated one of potassium permanganate (40 grams) is gradually added; after 12 hours heating on the water-bath, it is filtered, the filtrate acidified with acetic acid, and copper sulphate added, whereby an amorphous, blue salt separates; this is washed, and boiled with alkali and a few drops of ammonium sulphide, on acidifying the filtrate, the acid separates as a white, amorphous precipitate which melts at 137° with the evolution of gas and the formation of triazole, identical with Andreocci's pyrrodiazole (this vol., p. 637). The acid has therefore properties different from those of the pyrrodiazolecarboxylic acid described by Andreocci (*loc. cit.*), and it forms, in addition to the above-mentioned copper salt, a second one, which is a green, crystalline powder containing 2 mols. H_2O. A. R. L.

Synthesis of Closed Chains: Piperylbiguanide. By E. Bamberger and L. Seeberger (*Ber.*, **25**, 525—533).—By the action of potassium hydroxide on piperylbiguanide in chloroform solution for 8 to 10 days at ordinary temperatures, *piperylformoguanamine*, $C_5NH_{10}\cdot C\ll^{N\text{——}CH}_{N\cdot C(NH_2)}\gg N$, is formed, and is separated by removing the excess of chloroform, dissolving the residue in highly dilute

sulphuric acid, and precipitating the base with soda; on crystallisation from water or dilute alcohol, it is deposited in slender, lustrous prisms or needles melting at 194·5°. The compound resembles formoguanamine in general properties, and is either unacted on by acids and alkalis, or is decomposed with elimination of ammonia and piperidine. The *oxalate* is sparingly soluble; the *hydrochloride* crystallises from water or alcohol in small, colourless needles melting at 201° with previous softening at 100°. The *sulphate* is deposited in lustrous plates containing 1 mol. H_2O, and melts at 221—222°; the *picrate* forms yellow, dendritic needles which soften at 175° and melt at 188°. The *platinochloride* crystallises in orange-yellow, flat needles melting at 219° with decomposition; the *aurochloride* crystallises with difficulty in slender, yellow needles; it melts at 90°, and slowly undergoes decomposition at ordinary temperatures. The base yields two *argentonitrates;* the one has the formula $(C_8H_{13}N_5)_2,AgNO_3$, and is formed by mixing aqueous or alcoholic solutions of piperylformoguanamine and silver nitrate; it crystallises from water in colourless, concentric needles melting at 229—238° with decomposition; the second compound, $C_8H_{13}N_5,AgNO_3$, is amorphous, and is precipitated by the cautious addition of highly dilute ammonia to dilute solution in alcohol of its components. Piperylformoguanamine is also formed by heating anhydrous piperylbiguanide with half its weight of anhydrous sodium formate for a short time at about 160°. *Piperylacetoguanamine*, $C_5NH_{10}\cdot C<\begin{matrix}N---CMe\\ N\cdot C(NH_2)\end{matrix}>N$, is obtained in a similar manner by heating piperylbiguanide sulphate with sodium acetate at 190—200°, or together with ammeline, by heating piperylbiguanide acetate at about 215° (see below); it crystallises from alcohol in long, flat needles or small plates which melt at 177—179°; the yield is very small.

Piperylbiguanide acetate is prepared from the cupro-derivative, and crystallises in needles melting at 193°.

The authors explain the production of piperylformoguanamide from chloroform and piperylbiguanide by assuming that piperyldichloromethylbiguanide, $NH{:}C(NH_2)\cdot NH\cdot C(C_5NH_{10}){:}N\cdot CHCl_2$, is first formed, and changes spontaneously into a closed chain compound,

$$C_5NH_{10}\cdot C<\begin{matrix}N---CHCl\\ NH\cdot C(NH_2)\end{matrix}>N;$$

from this a molecule of hydrogen chloride is eliminated by the action of potash, giving rise to piperylformoguanamide. J. B. T.

Synthesis of Guanamine. By E. Bamberger and W. Dieckmann (*Ber.*, **25**, 534—542; compare preceding abstract).—Formoguanamine may be prepared by heating biguanide sulphate with anhydrous sodium formate at 150—200°, and also by the action of alcoholic potash and chloroform on biguanide hydrochloride. Isoamylguanamine can be obtained in a similar manner by heating biguanide caprate, or by fusing biguanide sulphate with sodium caprate for 1—1½ hours at 220—230°.

Acetoguanamine and ammeline are the sole products formed, the latter in larger proportion, by heating biguanide acetate at 230°; it is

also produced during the preparation of formoguanamine from guanidine formate.

Attempts to obtain tricyanogen derivatives from formic acid and formamidine, acetamidine, or benzamidine by a method analogous to Nencki's guanamine synthesis were fruitless.

The authors believe the production of formoguanamine from biguanide and chloroform to be preceded by the formation of the intermediate products $NH{:}C(NH_2)\cdot NH\cdot C(NH_2){:}N\cdot CHCl_2$ and

$$NH_2\cdot C\leqslant \begin{matrix} NH\cdot C(NH_2) \\ N\text{——}CHCl \end{matrix} \geqslant N,$$

and they regard the synthesis of guanamines from guanidine salts as consisting, in a condensation to the corresponding biguanide salt, which then, by dehydration, yields an intermediate compound, $NH{:}C(NH_2)\cdot NH\cdot C(NH_2){:}N\cdot CR{:}O$; this readily forms a closed chain, and finally a guanamine derivative $NH_2\cdot C<\begin{matrix} N\cdot C(NH_2) \\ N\text{——}CR \end{matrix}>N$, by the elimination of a second molecule of water. J. B. T.

Biguanide. By E. Bamberger and W. Dieckmann (*Ber.*, **25**, 543—546).—According to the explanation given by the authors of Nencki's guanamine synthesis (compare preceding abstract), the first step consists in the formation of biguanide and ammonia from guanidine. Anhydrous guanidine hydrochloride is heated in portions of 1 gram in an oil-bath at 180—185° for 3—4 minutes, the residue is dissolved in water, filtered in order to separate any ammeline which may have been formed, and the filtrate treated with cuprammonium sulphate solution; cuprobiguanide sulphate, $(C_2H_6N_5)_2,CuSO_4$, immediately separates in slender, lustrous, rose-coloured needles. The reaction proceeds so readily that it may be employed as a lecture demonstration.

The failure of Nencki and Rathke to obtain biguanide from guanidine was probably caused by their employing the free base or the carbonate.

The authors have investigated Smolkau and Friedrich's method of preparing biguanide; the best yield is obtained by intimately mixing anhydrous ammonium chloride (8 grams) with dicyanodiamide (5 grams), and heating at 195° for 5—10 minutes; the residue is extracted with water. *Biguanide picrate* crystallises from water in golden-yellow, lustrous, broad needles which melt at 232°, and are sparingly soluble. *Biguanide hydrogen sulphate* crystallises in lustrous, rhombic prisms, $a : b : c = 0{\cdot}5802 : 1 : 0{\cdot}3607$. J. B. T.

Alkaloïds of the Areca Nut. By E. Jahns (*Arch. Pharm.*, **229**, 669—707).—The coarsely-powdered areca nut was extracted three times with very dilute, cold sulphuric acid, the united extracts concentrated to about the same weight as the original material, and the alkaloïds precipitated with potassium bismuthoiodide, an excess of the latter being avoided, since it has a solvent action on the precipitate. The washed precipitate was then boiled with an excess of barium carbonate, the solution filtered, concentrated to a syrup, an

excess of barium hydroxide added, and the mixture repeatedly extracted with ether. The ether separates one alkaloïd, arecoline, which remains, after distilling off the ether, as a liquid.

The alkaline liquid remaining after exhaustion with ether was freed from barium and iodine by the addition of sulphuric acid and silver carbonate, the excess of silver and sulphuric acid precipitated by hydrogen sulphide and the cautious addition of barium hydroxide respectively, and the solution evaporated nearly to dryness. The residue was then exhausted with repeated quantities of absolute alcohol, which separates choline, whilst there remain three alkaloïds, arecaïne, arecaïdine, and guvacine. These three cannot be readily separated from one another by mere crystallisation. The arecaïdine was converted into arecoline (see below) by dissolving the mixture of the three alkaloïds in methyl alcohol and passing dry hydrogen chloride into the solution. The arecoline hydrochloride thus formed remains dissolved, whilst the hydrochlorides of the other two alkaloïds are almost insoluble. They were collected, and the bases liberated by the addition of silver carbonate. These were then separated from one another by dissolving the mixture of the two in hot water, and carefully adding absolute alcohol until crystallisation commenced, guvacine separating first. The process must, however, be repeated several times.

Arecoline, $C_8H_{13}NO_2$, was purified by converting it into the hydrobromide, recrystallising, liberating the base by the addition of solid potash, and extracting with ether. It is a colourless, odourless, strongly-alkaline, oily liquid, miscible in water, alcohol, ether, and chloroform, volatile with steam, and boiling at 209° with partial decomposition. Its normal salts are readily soluble, sometimes hygroscopic, but crystallisable. With potassium bismuthoiodide, they form a dark-red precipitate; with phosphomolybdic acid, a white precipitate; potassium mercury iodide precipitates a yellow, oily liquid which becomes gradually crystalline; iodine precipitates a brown liquid; picric acid, a tarry, gradually crystallising precipitate; auric chloride, a liquid which does not crystallise. Platinic chloride, mercuric chloride, and tannin produce no precipitates. The aqueous solution of the free alkaloïd is, however, precipitated by tannin.

Arecoline hydrobromide, $C_8H_{13}NO_2,HBr$, is readily soluble in water and in hot alcohol, less readily in cold alcohol. It forms long, thin, anhydrous prisms, permanent in the air, and melts at 167—168°. The *hydrochloride*, *sulphate*, *nitrate*, and *acetate* are crystalline, hygroscopic, and soluble in alcohol, water, and in a mixture of ether and alcohol; the *aurochloride*, $C_8H_{13}NO_2,HAuCl_4$, is a yellow, oily liquid, sparingly soluble in cold alcohol, more readily in hot alcohol; the *platinochloride*, $(C_8H_{13}NO_2)_2,H_2PtCl_6$, forms orange-red plates belonging to the rhombic system. (For the physiological properties of these alkaloïds, see Marmé, *Pharm. Zeit.*, 1889, 97; and Therap, *Monatsh.*, 1890.)

By heating arecoline with concentrated hydrochloric acid, either on the water-bath or in a sealed tube at 150°, arecaïdine and methyl chloride are formed. The same change is effected by hydriodic acid at a boiling heat, and concentrated alkalis act in a similar manner.

Arecaïdine, $C_{17}H_{11}NO_2 + H_2O$, was separated (see above) by converting it primarily into arecoline, which may be reconverted into arecaïdine by the methods just named. Boiling with barium hydroxide is the preferable method. It is recrystallised from 60 or 70 per cent. alcohol. It forms colourless, permanent crystals, readily soluble in water and in dilute alcohol, almost insoluble in absolute alcohol, insoluble in ether, chloroform, and benzene. The aqueous solution is neutral; with ferric chloride, it is coloured slightly red. It loses its water of combination at 100°, and melts at 223—224°. Its simple salts are crystalline, readily soluble in water, less readily in alcohol, and the solutions are acid. The *platinochloride*, $(C_7H_{11}NO_2)_2,H_2PtCl_6$, forms yellow octahedrons, and melts at 208—209°; the *aurochloride*, $C_7H_{11}NO_2,HAuCl_4$, decomposes when warmed with water; it melts at 197—198°.

Methylarecaïdine, $C_7H_{10}MeNO_2$, prepared by dissolving the alkaloid in methyl alcohol and passing dry hydrogen chloride into the solution, was found to be identical with arecoline.

The *ethyl* compound, *homarecoline*, $C_7H_{10}EtNO_2$, is prepared in the corresponding manner, and forms a colourless, strongly alkaline liquid, miscible with water, alcohol, and ether, and may be distilled with steam. It is poisonous, like arecoline. The simple salts resemble the corresponding arecoline salts. The aurochloride and the platinochloride are also similar.

Methylarecaïdine and ethylarecaïdine are salts of arecaïdine, this base containing a carboxyl group. The acid character of arecaïdine is, however, much less pronounced than its basic properties; it does not decompose carbonates readily, and its salts with the metals could not be obtained pure. When heated with barium hydroxide, methylamine is eliminated, indicating the presence of a methyl group attached to the nitrogen, and accordingly the formula $C_5NH_7Me{\cdot}COOH$ is assigned to arecaïdine, which thus would seem to be a tetrahydropyridine derivative. Attempts to remove the side chains and so arrive at pyridine proved fruitless. It may, however, readily be reduced and converted into a piperidine derivative by the action of sodium on the amyl alcohol solution. After the completion of the reaction, water is added, the amyl alcohol separated, the solution acidified with hydrochloric acid, and brought to dryness, extracted with alcohol, evaporated, water added, and the chlorine separated again by addition of silver oxide. The *dihydroarecaïdine* is then separated by chloroform and recrystallised from alcohol and ether. It forms very small crystals, readily soluble in water, alcohol, and chloroform, insoluble in ether; its solutions are neutral. Its formula is $C_7H_{13}NO_2 + H_2O$; it melts at 120°, but if first dried at 100°, the water separates, and the anhydrous base then melts at 162—163°. The *platinochloride* crystallises from ether-alcohol in anhydrous prisms, and melts at 215—216°. The *aurochloride* melts at 158—159°.

The *methyl salt*, *dihydroarecoline*, $C_5NH_9Me{\cdot}COOMe$, prepared by passing hydrogen chloride into the methyl alcohol solution, is, like arecoline, a colourless, strongly alkaline liquid, volatile with steam, and miscible with water, alcohol, and ether. The *hydrochloride* and *hydrobromide* are well characterised salts.

The constitution of these bases, arecaïdine, arecoline, and dihydroarecaïdine was eventually arrived at by synthesising them from methyltetrahydronicotinic acid. Methyl nicotinate was converted into methylnicotinic anhydride, and this was then reduced by tin and hydrochloric acid at the boiling temperature during one or two days. Both *methylhexahydronicotinic acid* and *methyltetrahydronicotinic acid* are formed, and are separated from one another by chloroform, the former being soluble. Methyltetrahydronicotinic acid,

$$C_5NH_7Me\cdot COOH,$$

is identical with arecaïdine; methylhexahydronicotinic acid,

$$C_5NH_9Me\cdot COOH\ [Me : COOH = 1 : 3],$$

is identical with dihydroarecaïdine, whilst methyl methyltetrahydronicotinate, $C_5NH_7Me\cdot COOMe$, is identical with arecoline.

Guvacine, $NH<\begin{matrix}CH_2---CO\\CH_2\cdot CHMe\end{matrix}>CO$, forms lustrous, colourless, permanent crystals, readily soluble in water, less soluble in dilute alcohol, insoluble in absolute alcohol, ether, chloroform, and benzene. The aqueous solution is neutral, and is coloured deep red by ferric chloride. It melts at 271—272° with decomposition. It has no action on the animal organism. Its salts are crystalline, soluble in water, of acid reaction, and insoluble in alcohol. The *hydrochloride* is anhydrous; the *platinochloride* crystallises with 4 mols. H_2O, which are liberated at 100°, and the salt melts a little above 210° with decomposition; the *aurochloride* is anhydrous, and melts at 194—195°.

Nitrosoguvacine, $C_6H_8NO_2\cdot NO$, prepared by heating the hydrochloride with sodium nitrite, is crystalline, sparingly soluble in cold water, readily soluble in hot water, fairly soluble in alcohol and ether. It is anhydrous, and melts at 167—168°. It gives Liebermann's nitroso-reaction, and does not colour a solution of potassium iodide and starch blue. No methyl *salt* could be prepared by treating the base in methyl alcohol with hydrogen chloride, thus showing the absence of the carboxyl group. It unites with potassium hydroxide as a phenol would do. Further, an *acetylguvacine*, $C_6H_8AcNO_2$, is obtained by treating guvacine with sodium acetate and acetic anhydride. It crystallises from absolute alcohol in anhydrous plates, and is sparingly soluble in cold water and alcohol; its solution is strongly acid.

Methylguvacine, $NMe<\begin{matrix}CH_2---CO\\CH_2\cdot CHMe\end{matrix}>CO$, is obtained by heating guvacine with sodium methoxide and an excess of potassium methyl sulphate at 140—150°. It forms a colourless, neutral, crystalline base, readily soluble in water and dilute alcohol, sparingly in hot absolute alcohol, and insoluble in cold alcohol. It crystallises with 1 mol. H_2O, which separates at 100°. It melts at 214—215°. Methylguvacine is identical with arecaïne. If it be heated with hydriodic acid at 150°, no change occurs, thus showing that the methyl group is not combined to the carbonyl group, but to the nitrogen. It is not strongly coloured by ferric chloride. It forms acid salts, readily soluble in water, less soluble in alcohol. The *platino-*

chloride forms orange-yellow, anhydrous, octahedrons, which melt at 213—214°; the aurochloride melts at 186—187°. J. W. L.

Cholic Acid and Dehydrocholic Acid. By Lassar-Cohn (*Ber.*, **25**, 803—811).—On heating potassium cholate with potassium hydroxide at a temperature of 245° (in amyl benzoate vapour), an amorphous acid is obtained, which probably has the formula $C_{19}H_{30}O_3$, and does not give a blue coloration with iodine. An amorphous product containing 33·6 per cent. of chlorine, is also formed by the action of phosphoric chloride on cholic acid in chloroform solution.

Dehydrocholic acid may be obtained by the oxidation of crude cholic acid; it combines with alcohol on warming, and consequently a pure preparation cannot be obtained by crystallisation from this solvent. The acid is readily deposited from a mixture of acetone and benzene, has the formula $C_{24}H_{34}O_5 + \frac{1}{2}C_6H_6$, and then melts at 239°; cholic acid, therefore, has the formula $C_{24}H_{40}O_5$. *Ethyl dehydrocholate* melts at 221°.

By the action of phosphoric chloride (4 mols.) on dehydrocholic acid (1 mol.) in chloroform solution, and treatment of the product with zinc-dust, a compound is formed which has the formula $C_{24}H_{32}O_3Cl_2$; it is proposed to term this *dichlorisodehydrocholal*. It crystallises from dilute alcohol, melts at 257°, and may be heated above its melting point without decomposition; the yield is one-seventh of the acid employed.

Isodehydrocholal, $C_{24}H_{34}O_5$, is obtained by dissolving the preceding compound in concentrated sulphuric acid, and adding water. It crystallises from alcohol, melts at 242°, has neither acid nor basic properties, and is isomeric with dehydrocholic acid.

The aqueous mother liquor obtained during the preparation of dichlorisodehydrocholal contains *chlorodehydrocholic acid*, $C_{24}H_{33}O_3Cl$; it is purified by means of the sodium and barium salts, crystallises from dilute acetic acid in thin plates, melts at 241°, and yields dehydrocholic acid on treatment with phosphorus and hydriodic acid. The *silver salt* is sparingly soluble. J. B. T.

Oxidation of Albumin in presence of Sulphur. By E. Rösing (*Chem. Centr.*, 1891, ii, 946—947).—When considerable quantities of an emulsion of pure sulphur are injected subcutaneously into dogs and rabbits, symptoms of hydrogen sulphide poisoning are developed. In investigating the cause of this, it was found that formation of hydrogen sulphide takes place when a current of air, hydrogen, or carbonic acid is aspirated through defibrinated animal blood mixed with the sulphur emulsion. The same occurs if the blood is diluted with 10 times its volume of water, but not if potassium ferricyanide or large quantities of sodium or potassium chloride are present, or if the blood has been previously boiled. With egg-albumin similar results are obtained. Doubtless the albumin is oxidised, a hydroxyl group, derived from a molecule of water replacing a hydrogen atom in the albumin molecule, whilst the displaced hydrogen atom unites with the remaining hydrogen atom of the water molecule and with an atom of sulphur to form hydrogen sulphide. In support

of this view it was shown that in the absence of water the formation of hydrogen sulphide does not take place, and it is hindered by the presence of neutral salts that can combine with water. And again if the albumin has been previously "hydroxylated" with ferricyanide, permanganate, or iodine solution, no hydrogen sulphide is formed; the same happens after a previous boiling of the albumin with water, hence a "hydroxylation" of albumin must take place when it is boiled with water. Parallel cases of oxidation may be observed with benzaldehyde and acetaldehyde; if these substances are mixed with sulphur and exposed to air and light, they oxidise, hydrogen being replaced by hydroxyl, and formation of hydrogen sulphide can be observed.

Many proteïds react in this way when mixed with sulphur; some at the ordinary temperature, some not until heated to 37°, or even to 100°. But most plant-proteïds do not react, neither do horn-shavings, human hair, α- and β-gluten, fibrin preserved in glycerol, hemi-albumose, nor peptone. On the other hand, it is remarkable that albumin, after it has been boiled with water, still forms hydrogen sulphide when digested with gastric juice. C. F. B.

Physiological Chemistry.

Influence of Amido-acids on Gastric Digestion. By E. Salkowski (*Virchow's Archiv*, **127**, 501—518).—In a previous communication (Abstr., 1891, 593), it was stated that although amido-acids, like glycocine and leucine, form loose combinations with hydrochloric acid, they have no important action on the digestive processes carried on by artificial gastric juice, and this has since been adversely criticised by T. Rosenheim (*Centr. klin. Med.*, 1891, No. 39), and F. A Hofmann (*ibid.*, No. 42). The former has used fibrin, the latter white of egg, and both find that the amido-acids very considerably lessen the activity of gastric juice. In the present research, fresh experiments are recorded in which it is found that the lessening when fibrin is used is almost negligible; with white of egg, it is greater, although not so great as Hofmann states. A factor which appears to influence the result is the amount of proteïd in proportion to the total volume of the digesting mixture. W. D. H.

Assimilation of Carbohydrates. By Hanriot and by A. Gautier (*Compt. rend.*, **114**, 371—374; 374—375).—Hanriot and Richet have shown previously that during the digestion of farinaceous food the coefficient of respiration rises, and may become greater than unity. Hanriot now finds that the coefficient exceeds unity whenever a fasting person is fed with a carbohydrate mixed with a large quantity of water. With 50 grams of glucose dissolved in 1000 c.c. of

water, the coefficient rose in every case to nearly 1·25. This increase in the coefficient is not affected by administration of capsules containing naphthol, and therefore is not due to intestinal fermentation.

Direct experiment shows that the oxygen absorbed, and the carbonic anhydride evolved, during the complete digestion of a known weight of glucose by a person previously fasting, are almost identical with the quantities calculated on the assumption that the glucose is directly converted into fat (that is, oleostearopalmitin), in accordance with the equation $13C_6H_{12}O_6 = C_{55}H_{104}O_6 + 23CO_2 + 26H_2O$. The time of conversion of the glucose is practically constant whatever the quantity of glucose absorbed, but with a quantity greater than 75 grams there is considerable oppression.

Gautier points out that Hanriot's experiments furnish conclusive proof that in many vital processes even warm-blooded animals behave like anaërobic organisms. His own researches on ptomaïnes established this point several years ago. The hydropyridic bases formed in the tissues, the extractive matters, and urea may be regarded as products of the anaërobic fermentation of the proteïds.

C. H. B.

Absorption of Carbonic Oxide by the Blood of a Living Mammifer. By N. Gréhant (*Compt. rend.*, **114**, 309—310).—Carbonic oxide dissolves in the blood corpuscles of living animals in accordance with Dalton's law. By means of his method the author was able to detect 1 part of carbonic oxide in 20,000 parts of the atmosphere of a carriage that had been heated for five hours with a briquette.

C. H. B.

Sugar in Blood. By J. Seegen (*Centr. Physiol*, **5**, 821—826, 869—872).—Bernard was the first to show that in drawn blood the sugar somewhat rapidly disappears. Lépine has recently attributed to this considerable importance, as he believes glycolysis occurs in the circulating blood, and is due to a ferment contained in the white corpuscles, but primarily formed in the blood by the pancreas. After extirpation, diabetes occurs, and this, according to Lépine, is the result of the absence of the glycolytic ferment.

In the present research, the fact that the sugar disappears when the blood is shed is fully confirmed; its disappearance is not influenced by the addition of chloroform, which, according to Salkowski, kills the organised ferments, but not the unorganised. Exclusion of bacteria by other methods does not prevent the disappearance of sugar. The ferment action is hindered by cold, occurs rapidly at 39—40°, and is destroyed at 54·5°. The conclusion is drawn that the ferment is formed by *post-mortem* changes in the blood.

W. D. H.

Excretion of Nitrogen in Kidney Disease. By H. Kornblum (*Virchow's Archiv*, **127**, 409—445).—Very complete observations are recorded, comparing the quantity and specific gravity of the urine, together with the nitrogen and phosphoric acid excreted in four cases

of Bright's disease with the normal. The food given was also analysed. The urine was collected and examined at intervals of six hours. In estimating the nitrogen in the urine, that contained in the albumin passed in the urine in such cases must also be taken into account. The main outcome of the examination is that in nephritis, although nitrogenous metabolism is slow, there is no actual diminution in the output of nitrogen as compared with that ingested.

W. D. H.

Urohæmatoporphyrin. By A. E. Garrod (*Lancet*, i, 1892, 793).—The pigment present in the urine of rheumatic patients rarely, if ever, imparts a characteristic colour to the urine; after separation of the pigment, however, it usually shows in an alkaline solution the five-banded spectrum described by MacMunn as characteristic of urohæmatoporphyrin. In some cases it appears to be ordinary hæmatoporphyrin, and in acid solutions gives the two-banded spectrum characteristic of that substance. The occurrence is quite independent of drug treatment.

In 14 out of 20 cases of chorea, the same urinary pigment was present. In these 14 cases there was either a rheumatic history or the presence of cardiac murmurs. In the remaining cases, where the pigment was absent, cardiac trouble and rheumatic history (personal and family) were both absent.

W. D. H.

Chemical Pathology of Diphtheria, Anthrax, and Infective Endocarditis. By S. Martin (*Brit. Med. J.*, i, 1892, 641—644, 696—701, 755—759).—Just as the gastric cells produce a soluble ferment which produces the effect called digestion, so, in infective diseases, the organism which is the primary infective agent produces a soluble ferment which, acting on the substance that it comes in contact with, produces digestive products from them. These digestive products are the poisons that produce the symptoms of the disease. In the case of the anthrax bacillus, the products of digestion are very similar to those of peptic and tryptic digestion; these are proteoses, peptones, leucine, tyrosine, and, in addition, an alkaloïd. The chief symptoms of anthrax are fever and coma. The proteoses are the fever producers; the alkaloïd is the coma producer.

These results which have been previously obtained pointed the way to the further investigation of other infective disorders; and the present papers deal especially with diphtheria and ulcerative endocarditis. The tissues examined were chiefly the blood and spleen; in the spleen, the products of diphtheritic digestion accumulate to a great extent. The poisons are chiefly proteïds of the proteose class, and associated with these is an organic acid of uncertain nature. The proteoses formed by the *Bacillus diphtheriæ* in artificial cultivation have in single and multiple doses the same physiological action as those found in cases of diphtheria in man. The *Bacillus diphtheriæ* is, therefore, the primary infective agent. The following table gives a scheme of what may be termed diphtheria digestion:—

Primary infective agent.	Secondary infective agent.	Digestive products.
Bacillus diphtheriæ	Diphtheria ferment (Roux and Yersin's poison) in membrane	Hetero-proteose, Proto-proteose, Deutero-proteose } in membrane. Organic acid ..... } in body.

A soluble ferment is liberated in the membrane which, when absorbed, digests the proteïds of the body, forming proteoses and an organic acid. The diphtheritic products do not all come from the membrane direct, as often the products are abundant in the blood and spleen, but only small flecks of membrane may be present. The proteïds are more or less stagnating in the spleen; hence they are readily digested, and, moreover, digestion goes further, resulting in the formation of deutero-proteose and the organic acid.

The physiological effects of the proteoses are fever, loss of weight, a loss of coagulability of the blood, and a transient, local œdema. There is, however, nothing specific about these symptoms. The specific result, especially if the poison is given in successive small doses, is the production of paralysis exactly like that which is so characteristic of diphtheria. The anatomical cause of this is found to be a degeneration of the peripheral nerves; the medullary sheath and, subsequently, the axis cylinder are affected. The organic acid causes the same nerve degeneration, but is not so toxic as the proteoses.

In ulcerative endocarditis, the spleen is again the repository and manufactory of the chemical poisons, which are proteoses, and of a non-proteïd residue which is strongly acid. These produce fever and wasting, but no paralysis or nerve degeneration. Fatty degeneration of the heart is found, but this occurs also in the case of the diphtheritic and anthrax poisons. A preliminary examination of the blood in a case of tetanus shows that chemical poisons of the same nature are present in that disease. W. D. H.

Impure Chloroform. By R. du Bois-Reymond (*Brit. Med. J.*, i, 1892, 209—214).—Pictet's new method of refining chloroform enables one to divide commercial chloroform into two parts, the pure material and the residue of foreign substances. Physiological experiments with these two substances led to the following results, which will be interesting to those who have followed the work of the Hyderabad Commission :—

1. The shape of the pulse waves and the frequency of respiration is about equally affected by both substances, the rate of respiration varying freely.

2. The pulse rate, compared in 19 cases, is higher at the close of the experiments with the residue than of those with pure chloroform.

3. The blood pressure in by far the greater number of experi-

ments at the moment the respiration stops is higher after inhalation of pure chloroform than after inhalation of the impure residue.

4. The residue causes stoppage of respiration much more quickly than pure chloroform. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Compounds accompanying Chlorophyll in Leaves. By A. Étard (*Compt. rend.*, **114**, 364—366).—Vine leaves gathered in July when treated with carbon bisulphide in the cold yield 3·7 per cent. of solid extract. This extract contains about 40 per cent. of a greenish plastic substance, insoluble in cold alcohol. It can be crystallised from ethyl acetate, melts at 74°, and boils at about 300°. It has the composition $C_{17}H_{34}O$, and the author gives it the name *vitole*. If the alcohol is expelled from the alcoholic solution of the carbon bisulphide extract, and the residue is agitated with dilute aqueous potash and ether, the ether dissolves a readily crystallisable substance, $C_{23}H_{42}(OH)_2$, *vitoglycol*, which yields a dibenzoic derivative. The potash solution contains semi-solid fatty acids. Possibly the function of the palmitic acid, which occurs constantly in leaves, is to limit the entrance of inorganic salts, and especially those of sodium, which are readily precipitated by potassium palmitate.

The carbon bisulphide extract of lucerne yields a large proportion of a white substance, which crystallises from ethyl acetate, melts at 80°, and boils at 395°, without sensible decomposition; with bromine, it yields a substitution derivative, but no additive compound. The compound has the composition $C_{20}H_{41}OH$, and yields a monobenzoic derivative; the author calls it *medicagol*. Direct experiment shows that medicagol passes unaltered through the alimentary canal of a horse when the latter is fed on lucerne.

Bryonia dioica, when treated in the same way, yields a hydrocarbon, $C_{20}H_{42}$, which crystallises in large, white lamellæ, melts at 69°, and boils without decomposition at 400°.

The compounds described constitute an important part of what is known as the *wax of leaves*. C. H. B.

Proteïds of Maize. By R. H. Chittenden and T. B. Osborne (*Amer. Chem. J.*, **13**, 529—552).—A further instalment of the work plotted out in the first paper (this vol., p. 379). The proteïd matter of the first class, namely, that soluble in 10 per cent. aqueous sodium chloride, but insoluble in water, may be resolved by fractional heat coagulation into three distinct globulins, two of which have much in common with phytomyosin and phytovitellin, although they are not identical with those substances.

The globulin which gradually coagulates when the temperature of a sodium chloride solution of the proteïds, prepared in the manner previously described, is slowly raised to 80°, contains relatively less nitrogen, the average percentage composition of several specimens made in this and other ways being:—C, 52·70; H, 7·02; N, 16·74;

S, 1·30; the nitrogen of the undifferentiated proteïd being 17·82 per cent. The globulin thus approximates closely in composition to animal myosin, which contains per cent.:—C, 52·82; H, 7·11; N, 16·77; S, 1·27; but the bulk of it coagulates at 70°, a temperature markedly different from the coagulation point of the myosin. The globulin also resembles the vegetable myosin which was obtained by Martin from papaw juice (Abstr., 1886, 642), and may thus be called *maize-myosin*. The tendency to coagulate at several different temperatures may be explained by assuming that maize-myosin undergoes a gradual change when heated, and this assumption accords with Martin's observation (Abstr., 1887, 507) that the myosins of wheat and rye are transformed into insoluble substances by heating their sodium chloride solutions at 35—40° for some time, and with Vines' view (*J. Physiol.*, **3**, 91—114) that phytovitellin may be transformed into phytomyosin. Maize-myosin is characterised by its solubility in cold, dilute, saline solutions, such, for instance, as those of the alkali phosphates naturally present in maize meal, and by taking advantage of this property may be extracted directly from the meal without dissolving the second globulin. The cold aqueous extract of the meal is saturated with ammonium sulphate, and the crude maize-myosin thus precipitated is successively treated with water and 10 per cent. aqueous sodium chloride. The mixed extracts are then dialysed in a stream of water, and the myosin thus precipitated is washed with water, alcohol, and ether, and dried.

The second globulin, *maize-vitellin*, which forms the bulk of the original proteïd matter, is obtained in small spheroïds when the solution from which the maize-myosin has been separated by heat coagulation is dialysed in a stream of water. Its solution in aqueous sodium chloride is coagulable by acetic acid, but not by heat, and it contains more nitrogen than the original proteïd matter, the average composition of several specimens prepared in this and other ways being:—C, 51·71; H, 6·83; N, 18·12; S, 0·86; thus closely approximating to that of the phyto-vitellin of pumpkin seeds:—C, 51·88; H, 7·51; N, 18·08; S, 0·60. It contains less sulphur than the myosin, and is, perhaps, as much akin to heteroalbumose as to the true globulins. Maize-vitellin is distinguished from maize-myosin by its solubility in weak, cold, saline solutions, and by its tendency to separate in spheroïdal form from sodium chloride solutions. It may, therefore, be extracted without the aid of heat coagulation from the crude proteïd matter, prepared in the manner previously described, or from the meal remaining after the extraction of the myosin. The proteïd matter, for example, is dissolved in 5 per cent. aqueous sodium chloride, and the vitellin is first precipitated by dilution with a large bulk of water, then redissolved by heating the whole to 45°, and finally caused to separate in spheroïdal form by cooling the solution slowly to 8°. The crude product thus obtained may be purified and caused to aggregate into larger spheroïds by repeating the treatment. Maize meal from which the myosin has been previously extracted by cold water may be treated with 10 per cent. aqueous sodium chloride, the crude vitellin precipitated by saturating the solution with ammonium sulphate, and purified by a somewhat long process, which comprises dissolving the crude product in sodium chloride

solution, reprecipitating it by dialysis, dissolving it again in salt solution, heating the solution to separate coagulable impurities, precipitating the now nearly pure product with acetic acid, redissolving the precipitate in sodium chloride solution, and, finally, precipitating the pure vitellin by dialysis.

The third globulin, which is characterised by its solubility in dilute solutions of salts other than chlorides, and its insolubility in water, is obtained by long-continued dialysis of the solutions from which the other globulins have already separated. It was not observed in the preliminary experiments, owing to the slow rate at which ammonium sulphate and the alkaline phosphates diffuse. This globulin has the composition C, 52·38; H, 6·82; N, 15·21; S, 1·26, and is thus distinct from the myosin and vitellin. It is further distinguished from these globulins by the low temperature, 62°, at which it is completely coagulated.

Various other substances isolated during the investigation were probably formed from the solutions by the incidental treatment, and do not exist as such in maize.

A substance, for instance, soluble in water, not coagulated by heat, and in general behaviour resembling the proteoses, was left in solution in the dialyser after the removal of the myosin and vitellin in the differentiation experiments first described. It did not exist in the original proteïd substance, since the latter did not yield any proteïd matter to boiling water; possibly it was formed by the hydrolysis of one of the less stable globulins.

Another substance, precipitated by the addition of a slight excess of very dilute hydrochloric acid to the sodium chloride solution of the undifferentiated proteïd matter, was possibly an acid globulin. It contained 17·39 per cent. of nitrogen.

The most prominent of these secondary products, however, are certain substances insoluble in aqueous sodium chloride, which are invariably formed during the dialysing operations by the prolonged action of the water or sodium chloride on the myosin or vitellin, which in this respect resemble animal myosin and certain vegetable globulins. When, for instance, the clear sodium chloride extract of maize meal is dialysed, the precipitated globulins are no longer completely soluble in sodium chloride solution; and the same thing happens when the globulins are precipitated by the addition of ammonium sulphate to the solution, especially if the sulphate is somewhat acid, although in the latter case the insoluble portion of the precipitate may contain the acid globulin mentioned above. In the early stages of transformation, these insoluble substances resemble the alkali albuminates, for they dissolve in dilute aqueous sodium carbonate, and are reprecipitated on neutralising the solution; but after more prolonged action they seem rather to resemble coagulated proteïd matters. Their composition is fairly uniform; the mean percentage composition, for instance, of the products formed by the action of aqueous ammonium sulphate or water on the sodium chloride or aqueous extracts of maize meal and subsequent purification was:—C, 53,45; H, 6·99; N, 16·11; S, 1·14; so that if these substances are formed from the globulin, the latter must undergo considerable modification. The change is not due to the

alkali used in the purification, since a specimen which had not been purified in this manner was found to contain the same percentage of nitrogen. Since this percentage is low, it is probable that the insoluble substances are formed from the myosin and the soluble globulin, and not from the vitellin, and it is probably this tendency of the first two to pass into such insoluble modifications which facilitates the purification of the vitellin. Jn. W.

Proteïds of Maize. By R. H. Chittenden and T. B. Osborne (*Amer. Chem. J.*, **14**, 20—40; compare this vol., p. 379, and preceding abstract).—An aqueous or sodium chloride extract of maize meal yields, after the three globulins and the soluble salts have been removed by dialysis, two albumins and a proteïd soluble in alcohol (proteose). The solution is treated with 10 per cent. of sodium chloride, and rendered slightly acid with 0·2 per cent. hydrochloric acid. The precipitated albumin (I) dissolves when washed with water, doubtless owing to the presence of hydrochloric acid; it is reprecipitated when the solution is carefully neutralised with dilute sodium carbonate, but dissolves in excess of the latter; after drying, this precipitate is no longer soluble in sodium carbonate.

The filtrate from I, when boiled, yields a coagulum of a second albumin (II); the portion first formed contains appreciably less nitrogen than the later portions.

The filtrate from (II) contains a proteose (III) which may be obtained by adding absolute alcohol to the concentrated solution. It is doubtful if these three substances all exist as such in the maize kernel; some of them may be formed in the processes used to separate them.

The maize meal, after extraction with water, contains another proteïd, *zeïn*, or *maize-fibrin* (IV), which can be extracted with warm 75 per cent. alcohol, and is precipitated when the alcoholic solution is poured into water. It is quite insoluble in 0·5 per cent. sodium carbonate, and in 0·2 per cent. hydrochloric acid; it dissolves in 0·2 per cent. aqueous potash, but is not converted into alkali-albumin, for the precipitate produced when the alkaline solution is neutralised is not soluble in excess of dilute acid, but dissolves in alcohol. It is converted, when warmed with water or dilute alcohol, into an insoluble variety, which, however, has the same chemical composition. Both of these varieties exhibit the ordinary proteïd reactions. The carbon-content of this proteïd is large.

The results of analyses of these substances are tabulated below:—

	I.	II.	III.	IV.
C	52·86—53·53	51·02—52·06	50·07—51·13	54·97—55·42
H	6·86— 6·79	6·57— 6·79	6·54—69·1	7·15— 7·35
N	15·69—15·41	17·28—15·78	15·88—16·59	16·01—16·31
S	1·48	25·75—24·64	2·37— 1·62	0·53— 0·67
O	23·26		24·52—23·75	21·05—20·52

C. F. B.

Phosphoric Acid in Soil and its Estimation. By C. L. Wiklund (*Landw. Jahrb.*, **20**, 909—928).—The attempts which have been made to ascertain the fertility of soils by analysis have met with little success, owing, largely, to the want of vegetation experiments showing the physiological value of the nutritive matters dissolved by the various reagents. Of all soils, the peaty soils seem most likely, when subjected to total analysis, to yield results which would indicate fertility, such soils being almost wholly derived from plant residues. For this reason it has been usual to determine the total amount of ash constituents in such soils. As regards sulphates and phosphates, however, the amounts found in the ashes do not represent the amounts pre-existing in the soils, being partly formed from sulphur and phosphorus present in other forms in the soil (compare Eggertz and Nilson, Abstr., 1890, 192; Berthelot and André, Abstr., 1888, 384). Nilson and Eggertz's method, which is generally used in Sweden, consists in treating the powdered soil, at the ordinary temperature, with 4 per cent. hydrochloric acid for 48 hours (using for 1 gram of dry soil 10 c.c. of acid), and analysing the filtrate in the usual manner.

The author describes a number of experiments made with the Eggertz-Nilson method. The results show that the method gives too low results with peaty soils containing much lime or ferric oxide; in the case of a sample containing 35·49 per cent. of lime and 0·35 per cent. of phosphoric acid, no phosphates were extracted at all. Such soils require either stronger acid, or repeated extraction with 4 per cent. acid, to remove all the soluble phosphates. It can also not be considered as proved that the amount of phosphoric acid dissolved by the method is the maximum assimilable amount for all plants. The amount of phosphoric acid found by the method will not show whether the soil requires manure for any particular kind of plant. A soil extracted by 4 per cent. acid may be rendered unsuitable for the growth of one plant, and yet contain sufficient phosphates for another.

In order to ascertain the relation between the amounts of phosphates dissolved by 4 and by 12 per cent. acid, and the amount found in the burnt soils, 47 different peaty soils were examined. The results show that, in some peaty soils, the greater part of the phosphorus exists as phosphoric acid; but in most of those examined the amount of pre-existing phosphates was much less than that of the burnt soils. In the case of soils which did not contain much lime or ferric oxide, the amounts of phosphates extracted by 4 and by 12 per cent. acid were essentially the same, showing that the stronger acid does not liberate phosphoric acid from the organic matter of the soil.

With regard to the question as to the manner in which the phosphoric acid is combined, several of the soils were extracted with 10 per cent. acetic acid, and the results compared with those obtained with dilute hydrochloric acid. Most of the pre-existing phosphate was found to be insoluble in acetic acid, and is, therefore, probably, in combination with iron.

In order to ascertain the amount of phosphorus in the substance extracted from soils by 5 per cent. ammonia (Grandeau's "matière

noire"), three samples of soils were three times extracted with 4 per cent. hydrochloric acid and then with ammonia (10 c.c. to 1 gram of dry soil), and the extract precipitated with hydrochloric acid. The dried "matière noire" from the three samples contained 0·553, 0·409, and 0·200 per cent. of phosphoric acid respectively, and the amounts shown as percentages in the original soil will be 0·040, 0·049, and 0·020. Practically the same results were obtained (with two of the samples) when the soils were only once extracted with 4 per cent. acid (and were known to still contain phosphates) before extracting with ammonia. The results confirm those of Eggertz, that "matière noire" does contain phosphorus. N. H. M.

Analytical Chemistry.

Asbestos in Filtration. By W. P. Barba (*Chem News*, 65, 101).—To aid filtration it is recommended to add finely-divided asbestos, suspended in a suitable liquid, to the freshly-precipitated troublesome precipitate, and then to collect on an asbestos plug. The precipitate may then be washed, redissolved, and titrated with great ease. D. A. L.

Estimation of Nitrogen. By E. B. Voorhees (*Chem. News*, 65, 99—100, 111—112).—As reporter to the Association of Official Agricultural Chemists, Washington, the author records the results of the analysis of the following test mixtures sent to various chemists:—1. A mixture of 400 grams of potassium nitrate and 56 grams of sodium nitrate. 2. A mixture of 250 grams of linseed meal, 250 grams of cotton-seed meal, and 100 grams of sodium nitrate. 3. A mixture of 300 grams each of dried blood and ammonite. By far the majority of the analyses were made by the Kjeldahl method, modified for nitrates when necessary, and taken all round, the results are satisfactory; a few analyses were made by the soda-lime and Ruffle methods, the former giving results practically identical with the Kjeldahl results, whilst the Ruffle results were lower, but were too few for a fair comparison. Test experiments using 2 grams of zinc sulphide and 1 gram of salicylic acid instead of 2 grams of zinc-dust and 2 grams of salicylic acid have proved satisfactory, and therefore the adoption of this modification is recommended, because the zinc sulphide can all be added at once, and so saves trouble; the oxidation too is more rapid, and as less salts are present, the distillation is quieter. It is further recommended to digest in and distil from the same flask, and to use metallic mercury instead of mercuric oxide. D. A. L.

Estimation of Nitrous Acid. By A. G. Green and F. Evershed (*Chem. News*, 65, 100—101).—The authors point out that Lunge in condemning the diazotisation method of estimating nitrous acid, has only tried Schultz' modification and not the method suggested by the

authors (Abstr., 1887, 396), in which normal aniline hydrochloride solution is titrated, in a flask surrounded by ice and water, with a normal solution of the nitrite, using zinc iodide and starch solution as an indicator. D. A. L.

Oxidation of Arsenic by the Electric Current. By L. K. Frankel (*Chem. News*, **65**, 54—57, 66—68).—Stimulated by the good results obtained by E. F. Smith in the oxidation of sulphides by the electric current (Abstr., 1890, 1342), the author has tried, with success, the oxidation of arseniferous minerals by means of the same agency. His general mode of procedure has been to drop the pulverised mineral into fused potash contained in a nickel crucible, attached to the positive pole of an electric circuit, a platinum wire, dipping in the molten potash, serving for the other electrode, and when sufficiently electrolysed, to disintegrate the mass with water, filter, acidify with hydrochloric acid, render strongly alkaline with ammonia, and again filter. The arsenic is then precipitated as ammonium magnesium arsenate, collected on a Gooch crucible, and weighed as pyroarsenate.

In the case of gersdorfite, niccolite, arsenopyrite, cobaltite, and proustite, about 25—30 grams of potash is used for from 0·2 to 0·3 gram of mineral, and a current of 1 ampère is passed for from 20 to 30 minutes, reversing the current at the end for 3—5 minutes, to remove any particles of mineral retained by the deposit on the cathode.

With free arsenic or orpiment, when loss by volatilisation has to be avoided, the molten potash is allowed to cool down so as just to let the current pass, the powdered metal or mineral is then spread over the surface, and, if necessary, a very small flame is applied to reinstate conductivity. In 10 minutes the temperature of the mass is raised, and a current of 1 ampère sustained for 25 minutes, reversing for five minutes at the end. With rammelsbergite, chloanthite, and smaltite, a larger quantity, 40 grams, of potash and a longer time, 45 minutes, with in the case of rammelsbergite 3-minute reversals after each 10 minutes, were required to effect the oxidation of the arsenic. Thus these arsenical minerals show some analogy to the sulphides in their behaviour under the above treatment; ferrous sulphide was observed by E. F. Smith to oxidise more readily than iron pyrites, and now the author finds that minerals with 1 atom of arsenic in the molecule are more readily decomposed than those containing 2 atoms of arsenic in the molecule. Domeykite and enargite are also amenable to this treatment.

With regard to the estimation of the arsenic, neither weighing as sulphide nor collecting the ammonium magnesium arsenate on paper filters was found satisfactory, nor did Pearce's method of estimating as silver arsenate in a carefully neutralised solution of an alkaline arsenate, prove successful in the author's hands. As, however, the precipitation of ammonium magnesium arsenate is slow in the presence of much alkali, it is sometimes advantageous to reduce with sulphurous acid, precipitate as arsenious sulphide, and subsequently reconvert into arsenic acid, and weigh as magnesium pyroarsenate.

In the treatment of sulphides, E. F. Smith noticed the transition of the sulphur through the stages hydrogen sulphide, sulphurous anhydride, and finally sulphuric anhydride. No such phases have been noticed in the behaviour of arsenic in the above experiments.

D. A. L.

Estimation of Phosphoric Acid in Soils. By C. L. Wiklund (*Landw. Jahrb.*, **20**, 909—928).—See this vol., p. 750.

Estimation of Sulphur in Red Copper. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **10**, 125).—The method proposed by Fresenius is not available, since barium nitrate does not precipitate small quantities of free sulphuric acid in copper nitrate solutions. The author dissolves 25 grams of the copper in nitric acid and electrolyses the solution until about 20 grams are deposited, he then evaporates the liquor to remove the excess of nitric acid, and again electrolyses until the whole of the copper is deposited; the sulphuric acid is then estimated in the copper-free liquid. As pointed out by v. Meyer, the employment of a gas flame in the evaporation is objectionable on account of the likelihood of sulphurous contamination. T. G. N.

New Method of Organic Analysis. By Berthelot (*Compt. rend.*, **114**, 317—318).—The substance is burnt in compressed oxygen in the calorimetric bomb, the heat developed being measured if desired. The gases in the bomb are then allowed to pass through tubes containing pumice moistened with sulphuric acid, and through tubes containing solid potash or potash solution. The residual gas is extracted by means of a pump, pure air is allowed to enter, this in its turn is extracted, and the process is repeated two or three times. When an estimation of the hydrogen is required, dry oxygen must be used, and the bomb must be heated before the operation in order to expel the moisture derived from previous experiments. Allowance must be made for the traces of nitric acid formed during combustion, since they volatilise with the water. In the case of compounds containing sulphur, a small quantity of water is placed in the bomb before the experiment, and the whole of the sulphur remains in solution in the form of sulphuric acid. Phosphorus may be estimated in a similar way. C. H. B.

Electrolytic Estimation of Metals as Amalgams. By W. Gibbs (*Amer. Chem. J.*, **13**, 570—571).—The author points out that his experiments on the electrolytic separation of certain metals from solutions of their salts by means of mercury cathodes and platinum anodes (*Nat. Acad. Sciences*, October, 1883) were purely qualitative. He thinks, however, that the method should be applicable to the estimation not only of the metals, but also of the electronegative elements or radicles with which they may be combined. Jn. W.

Estimation of Copper by De Haen's (Brown's) Method. By C. A. Lobry de Bruyn and F. H. Van Leent (*Rec. Trav. Chim.*, **10**, 119—124).—The authors publish data of the determination of copper in pure copper sulphate and in alloys by De Haen's method,

and compare the results with those obtained electrolytically and by precipitation as copper sulphide. By well shaking the not too dilute copper solution with 5 c.c. of potassium iodide solution (20 per cent.) in a 500 c.c. stoppered flask for 5—10 minutes, adding the greater part of the sodium thiosulphate solution, whilst preventing undue access of air, then adding starch solution, and determining the end of the reaction by the change of the dirty-blue coloration to a cream-yellow on subsequent addition of thiosulphate, concordant results are obtained which do not differ by more than 0·1 per cent. from the calculated percentage. The presence of free acid, of nickel, manganese, and iron sulphates does not affect the results, nor does lead nitrate, but bismuth nitrate masks the end of the reaction, owing to formation of bismuthous iodide, and the results are low.

In the case of alloys, 0·3—0·4 gram is dissolved in dilute nitric acid, and 1 c.c. of sulphuric acid (sp. gr. 1·4) is added, the whole is then evaporated to dryness on a water-bath, and the residue dissolved in water is treated as above described (compare Westmoreland, Abstr., 1887, 80). T. G. N.

Quantitative Separation of the Metals of the Hydrogen Sulphide Group by means of Bromine Vapour. By P. Jannasch and P. Etz (*Ber.*, **25**, 736—741; compare this vol., pp. 385 and 540).—Wood's metal, containing bismuth, lead, tin, and cadmium in the proportion 15 : 8 : 4 : 3 respectively (1 gram) is dissolved in *aqua regia*, the solution evaporated to dryness, the chlorides redissolved in dilute hydrochloric acid, and a current of hydrogen sulphide passed through the boiling solution for about half an hour; the sulphides are then collected on a tared filter, dried at 100°, and subsequently cautiously heated in a boat as described (*loc. cit.*) in a current of air containing bromine vapour, when stannic and bismuth bromides volatilise, and are condensed in dilute nitric acid, whilst a fused mixture of lead and cadmium bromides remains, and is allowed to cool in a current of the same gaseous mixture. A slight sublimate of lead chloride is sometimes found on the upper portion of the combustion tube when commercial bromine is employed. The fused bromides are repeatedly evaporated with chlorine-water on the water-bath, the resulting chlorides dissolved in water, and the lead and cadmium estimated as sulphate and oxide respectively. The nitric acid containing the tin and bismuth is evaporated on the water-bath with fresh quantities of nitric acid, the tin being weighed as stannic oxide, and in the filtrate, from which the excess of nitric acid is removed by boiling, the bismuth is precipitated with ammonium carbonate, and weighed as oxide, the latter, when necessary, being separated from silica, derived from the porcelain vessels, by a second precipitation. Good results are obtained.

The following method is much quicker and quite as accurate. The alloy is mixed with sulphur, and the mixture heated in a porcelain boat in a current of carbonic anhydride; after volatilising the excess of sulphur, the operation is repeated, if necessary, and the mixed sulphides treated with bromine vapour as above described. The complete analysis occupies from one and a half to two days.

A. R. L.

Estimation of Iron and Aluminium by the Glaser Method. By B. H. Gibbins (*Chem. News*, **65**, 51).—Referring to a suggestion made by Teschemacher and Smith in connection with the Glaser method for the estimation of iron and aluminium (Abstr., 1890, 420), the author remarks that in this method, even when 25 per cent. of magnesia is present, there is no fear of precipitating any ammonium magnesium phosphate, from the alcoholic solution, by adding ammonia carefully and in only slight excess; he therefore adopts the following procedure:—An aliquot part of the alcoholic solution is neutralised with ammonia (sp. gr. 0·96), the alcohol is driven off over a steam-bath, without evaporating to dryness, water and a few drops of ammonia are then added, the whole boiled vigorously, cooled rapidly, and the iron and aluminium phosphates filtered off without delay. In the presence of manganese, the precipitate is redissolved in dilute nitric acid, and the solution treated with ammonium phosphate, and neutralised with ammonia; a precipitate free from manganese is then obtained. D. A. L.

Estimation of Iron and Aluminium in the presence of Phosphoric Acid. By W. H. Krug (*Chem. News*, **65**, 68—69, 78—79, 89—90, 98—99).—The author has compared the various methods proposed for the estimation of iron and aluminium in the presence of phosphoric acid, and finds that the molybdate methods give oxides of iron and aluminium contaminated with molybdic anhydride; whilst in the alcohol methods, the results are vitiated either by the inclusion of calcium sulphate in the oxides, as in the Glaser method, or by the retention of oxides by the calcium sulphate, as in the Jones method. In the latter case, the quantity of iron oxide retained not alone increases with the amount of iron present, but is also augmented by the precipitation of iron as an alum, when potassium, or, to a less extent, when ammonium, salts are present. The following modification of the molybdate method is stated to be free from all the above defects, and is, moreover, short and rapid:—100 c.c. (1 gram of substance) of a nitric acid solution is mixed with ammonium molybdate and some ammonium nitrate, and, after remaining over night, is filtered. 200 c.c. of the filtrate containing ammonium nitrate is cautiously precipitated in the cold with ammonia, the precipitate is washed, redissolved in a few c.c. of a solution of ammonium nitrate in dilute nitric acid, reprecipitated with ammonia, filtered, washed, ignited, and weighed. In this way the oxides of iron and aluminium are obtained free from molybdic anhydride, and the iron can be readily determined in the usual way. D. A. L.

Reactions of Hydrastine and other Alkaloïds. By D. Vitali (*L'Orosi*, **14**, 405—416).—If a small crystal of hydrastine, or of one of its salts, is placed on a porcelain capsule and covered with concentrated sulphuric acid (0·5—1 c.c.), it turns yellow, and, on stirring, the liquid acquires the same colour; on adding a small fragment of nitre (an excess must be avoided), the colour changes to a more or less intense brownish-yellow; if a solution of stannous chloride is now added drop by drop, the solution acquires a magnificent, reddish-

violet colour, the intensity of which depends on the amount of alkaloïd present. This coloration is not destroyed on dilution with water.

If a particle of hydrastine is treated with nitric acid (4 to 6 drops), the alkaloïd turns yellow; on heating for an instant to the boiling point, nitrous fumes are evolved, and, on evaporating to dryness at a gentle heat, a yellowish residue is left which, when cold, is coloured brownish-yellow by alcoholic potash, and remains as a greenish-brown mass on evaporating the alcohol. When cold, this becomes deep-violet on treatment with sulphuric acid. Solutions of hydrastine must be evaporated to dryness before applying the tests, which are sufficiently delicate to detect 0·0001 gram of the alkaloïd.

Bebeerine turns blood-red on treatment as described with concentrated sulphuric acid and nitre, the colour changing to green on the addition of stannous chloride.

Codeïne turns dark brick-red when alcoholic potash is added to its solution after treatment with nitric acid, and coffee-coloured when further treated with sulphuric acid; similarly, *narcotine* acquires an orange colour on the addition of potash, the colour changing to violet-red on adding sulphuric acid, and red to yellow on diluting with water.

A rather less delicate test for hydrastine is as follows:—A particle of the solid alkaloïd is fused with five or six times it weight of caustic potash, the melt allowed to cool, acidified with hydrochloric acid, extracted with chloroform, the extract evaporated to dryness on the water-bath, and the residue treated with a very dilute solution of ferric chloride; a fine, blue coloration is obtained if a few milligrams of the alkaloïd has been employed; the colour is destroyed by acids, and changed to brownish-red by alkalis.

A characteristic reaction for *aconitine* is obtained by adding to it in small quantities a solution of potassium permanganate in sulphuric acid (1 : 200) and stirring; the green colour of the reagent is replaced by a violet-tint which disappears on further agitation, and is restored on adding more of the reagent, and so on. A point is ultimately reached at which the colour is not affected by agitation, but at once disappears on diluting with water.

Clear indications of the presence of hydrastine in putrid animal matter cannot be obtained if the latter is treated by the Stas-Otto method, on account of the ptomaïnes and other impurities contained in the extract. Hydrastine is however extracted from alkaline, but not from acid, solutions by light petroleum, and, by taking advantage of this fact and substituting baryta for sodium carbonate, and light petroleum for ether, in the extraction, it is possible to isolate the alkaloïd in a state of sufficient purity. The author recommends the use of light petroleum in place of chloroform, ether, or amyl alcohol in the extraction of alkaloïds from urine and animal remains, as they are nearly all soluble in that menstruum (the exceptions are morphine, curarine, and pilocarpine) whilst ptomaïnes, leucomaïnes, pigments, and extractive matters are insoluble. S. B. A. A.

General and Physical Chemistry.

Refractive Powers of Isocyanides and Nitriles. By T. Costa (*Gazzetta*, **22**, i, 104—109).—A comparison of the refractive powers of the isomeric nitriles and isocyanides might be expected to show whether in the latter class of substances the carbon atom in the CN group is bi- or quadri-valent. The author has examined ethyl isocyanide, propionitrile, and benzonitrile; his results are contained in the following table:—

	n_α.	n_β.	n_γ.	Molecular refraction.
Ethyl isocyanide....	1·35870	1·36569	1·36999	16·26
Propionitrile	1·36314	1·36925	1·37309	15·64
Benzonitrile	1·52555	1·54494	1·55721	31·33

The molecular refraction is calculated by means of the formula $\frac{M(n_\alpha^2 - 1)}{d(n_\alpha^2 + 2)}$. The molecular refraction of ethyl isocyanide will be seen to be somewhat higher than that of its isomeride, propionitrile. The carbon atom in the CN group must therefore be supposed to be saturated, and the isocyanide should hence have either the constitution C≡N·X or X·N:C:C:N·X. The author has endeavoured to determine the molecular weight of ethyl isocyanide by the cryoscopic method, using benzene as the solvent. On cooling, however, the isocyanide separates, forming an emulsion, and renders the experiment futile.

W. J. P.

Absorbent Power of Coloured Salts and Electrolytic Dissociation. By G. Magnanini (*Gazzetta*, **22**, i, 131—140).—The author criticises unfavourably the deductions drawn by Knoblauch (*Wied. Ann.*, **43**, 738) from observations made on the absorption spectra of solutions of coloured salts. Knoblauch concluded that on varying the degree of concentration of the coloured salt solution no change in the absorption spectrum occurred; no photometric measurements were made, however, and the spectra were simply compared by the eye. As, however the most concentrated solutions used by Knoblauch contained the salt in a considerably dissociated condition, mere inspection of the absorption spectra could not be expected to afford any criterion of the progress of dissociation as the solution became more dilute. Knoblauch's conclusion, that his experiments are in disaccord with the electrolytic dissociation hypothesis, is therefore unfounded.

The author has measured the extinctions for solutions of various coloured salts, reducing the electrolytic dissociation of the dissolved salt by adding to the solution a colourless salt or free acid having one ion in common with the coloured salt. Thus, to solutions of copper sulphate were added considerable proportions of sodium sulphate and sulphuric acid. The coefficients of extinction in this

and similar cases were found to be unaltered by the decrease in the electrolytic dissociation. The author concludes that for the salts examined, that is, copper sulphate and nitrate, nickel sulphate, and potassium permanganate, the colour of the aqueous solution is independent of the electrolytic dissociation. W. J. P.

Molecular Dissymmetry. By P. A. Guye (*Chem. Centr.*, 1892, i, 10; from *Arch. sci. phys. nat. Geneva* [3], **26**, 333—369).—In addition to the examples which the author has already given (this vol., p. 399) in proof of the correctness of the symmetrical and unsymmetrical arrangement of the groups of atoms in relation to the carbon atom, he now names derivatives of tartaric, malonic, aspartic, lactic, and malic acids, of leucine, and phenyl mercaptan. Exceptions occur in the case of glutamic acid, the constitution of which is not certain, and in those of some asymmetrical compounds the groups of which have approximately equal masses.

J. W. L.

Stereochemistry of Diacetyltartaric Acid. By A. Colson (*Compt. rend.*, **114**, 175—178).—Diacetyltartaric acid has been obtained by the author in the crystalline form, with 3 mols. H_2O. It fuses at 58°, is very deliquescent and soluble in water, alcohol, and ether, less soluble in benzene. In these four solvents it rotates the plane of polarisation to the left, although it is derived from dextrorotatory tartaric acid. Its salts are lævorotatory in aqueous solution.

It may be obtained in the crystalline form:—(1) By allowing diacetyltartaric anhydride to deliquesce, taking up with dry ether, and slowly evaporating in dry air. By this means rhomboidal, almost square, tables are obtained. (2) By treating the anhydride with ether saturated with water, and slowly evaporating the ether.

The conversion of the dextrorotatory tartaric acid into a lævorotatory compound is not due to the heat evolved during the formation of the latter, for dextrorotatory tartaric acid is regenerated by slow hydrolysis through the action of the moisture of the air. The optical inversion is due to the action of the inactive acetic acid. It is concluded that an inactive substance such as water may affect the rotatory power, but the tetrahedron formula fails to indicate this. The tetravalency of carbon, founded on the Le Bel-Van't Hoff notation, excludes also molecular combinations such as the crystallised acid described.

According to Guye's method of accounting for diacetyltartaric acid being lævorotatory, on the assumption of the tetrahedron formula the diacetyltartrates should be dextrorotatory, whereas they are lævorotatory. According to Guye, diacetyltartaric anhydride should be more strongly lævorotatory than the acid; on the contrary, it is dextrorotatory.

The conclusion is therefore drawn that the chemical notation based on the properties of the regular tetrahedron is insufficient to represent the constitution of active substances, and may lead to inaccurate predictions. W. T.

Stereochemistry and the Laws of Rotatory Power. By P. A. Guye (*Compt. rend.*, **114**, 473—476).—A reply to some objections recently brought by Colson (preceding abstract) against the author's method of calculating the sign of the rotatory power of carbon compounds. The method was not intended to be applied to ring compounds, on account of the uncertainty as to the amount of deformation of the angles of the tetrahedra in the molecules of such compounds. As the particular compound, diacetyltartaric anhydride, which Colson selects in illustration of his argument, is a ring compound, his conclusions are necessarily invalid. Jn. W.

Coexistence of Dielectric Power and Electrolytic Conductivity. By E. Bouty (*Compt. rend.*, **114**, 533—535).—The measurements were made by the method previously employed to determine the dielectric constant of mica at high temperatures. The dielectric constant for pure terebenthene was found to be 2·25, which is exactly the mean of the determinations of Silow, Quincke, Palaz, and Negreano. The conductivity of distilled water is so great that the measurements of time cannot be made with sufficient accuracy. The determination of the dielectric constant of ice, however, presents no great difficulty, and the value of the constant is found to be 78 at −23°. As the temperature rises, the conductivity increases rapidly, but the dielectric constant shows no appreciable variation. The constant remains the same even if a small quantity of sodium chloride is added to the water before freezing, or if river water is used instead of distilled water. It follows that dielectric power and electrolytic conductivity may coexist in the same substance, the former remaining practically constant, whilst the latter varies within wide limits.

C. H. B.

Galvanic Polarisation at Small Electrodes. By K. R. Koch and A. Wüllner (*Ann. Phys. Chem.* [2], **45**, 475—507; 759—797).—Fromme found that with great current density strong polarisation appeared at small electrodes (Abstr., 1890, 316, 675). Richarz, on the other hand, concluded that the polarisation does not alter with the current density, but that the resistance in the electrolyte does. (Abstr., 1890, 676). The authors have investigated the question afresh, using a new method of measurement. They observed simultaneously the current strength, the difference of potential of the electrodes, and also, by an electrometric method, the polarisation at each electrode. From the data, the resistance of the electrolytic cell could be calculated. Their results with solutions of sulphuric acid of various strengths, and with electrodes of different sizes and shapes, are given in numerous tables.

In the second portion of their paper, the authors give an account of their investigations on the phenomena of "current reversal" (sudden reduction of the direct current and increase of polarisation), produced by increasing the current strength beyond a certain limit. The results obtained with various solutions and electrodes are given in tabular form; and figures, after instantaneous photographs, show the evolution of gas, &c., at the electrodes, with the current below and above the limit for reversal.

The authors state the conclusions at which they have arrived, as follows:—

1. There is, at short electrodes of platinum wire in dilute sulphuric acid, a polarisation which increases considerably with the current strength.

2. This polarisation is due to an electromotive force opposed to that of the direct current, and to the resistance of a badly conducting layer which is formed round the electrodes. The electromotive force of polarisation is not dependent on the length of the wire electrodes, or, in general, on the concentration of the solution; and has the value to which the polarisation of large electrodes approximates with increasing current density, namely, 3·79 volts.

3. The resistance of the transitional layer is independent of the current strength with a given electrode and a given solution. For the same pair of electrodes it is proportional to the specific resistance of the solution; and for the same solution it diminishes as the length of the wire electrodes increases.

4. These rules are only valid for current strengths below a certain limit, which depends on the length of the electrodes and on the conductivity of the solution. When this limit is reached, an increase of the electromotive force causes a "reversal"; by the sudden increase of polarisation at the smaller electrode, the current becomes very weak. The strength of the residual current is not increased by an augmentation of the electromotive force, and is greater for long than for short wire electrodes.

5. If the reversal is caused by the great polarisation at the anode, this electrode becomes incandescent, sometimes splits, and is rapidly destroyed. If the seat of the reversal is at the cathode, a bluish-white glow, due to a gaseous envelope, surrounds this electrode, which may itself become incandescent. It is, however, not destroyed.

6. Zinc electrodes in zinc sulphate solution and copper electrodes in cupric sulphate solution exhibit, likewise, a polarisation which increases with the current strength. At a certain current strength a sudden increase of the polarisation at the anode take place; and this great polarisation can be obtained at large anodes with small current density by producing it first at a small portion of the surface by means of a large current density. J. W.

Electro-capillary Phenomena. By Gouy (*Compt. rend.*, **114**, 211—214).—If a dilute solution of sulphuric acid is taken, and with the capillary electrometer the law determined which connects the height of the mercurial column with the polarisation of the meniscus, on taking the polarisations as abscissæ and the heights as ordinates, the well-known parabolic curve of Lippmann is obtained. If iodide of potassium is substituted for sulphuric acid, the maximum is found to be less, and the portion of the curve during which the capillary meniscus plays the part of the anode, or the anodic portion, is steeper in the case of the sulphuric acid, or, in other words, the electrometer is more sensitive with this liquid. It follows from this that the two curves cannot be made to coincide by moving them along the axis of abscissæ, but by this means it is found that their cathodic portions

can be made to coincide at a short distance below the maximum. The same is true of other potassium salts besides the iodide. The reason for this is very evident. On the anodic side, the surface tension will depend on the nature of the mercury compound, oxide, iodide, &c., which tends to form, but at the cathode, hydrogen alone is liberated in the above cases. H. C.

Optical Measurement of High Temperatures. By H. Le Chatelier (*Compt. rend.*, **114**, 214—216).—The author recommends for the measurement of high temperatures, the photometric determination of the light emitted from a substance at the temperature under observation. The principal difficulties are, that the intensity of the radiation from such a substance depends not only on its temperature but also on its chemical nature, the physical condition of its surface, and the temperature of the substances which surround it. In cases where its diffusive power is nothing, the radiation is independent of the temperature of its surroundings, and depends only on its own temperature. This is the case with the magnetic oxide of iron, and carbon. The emissive power of other substances may be checked, as the author shows, by reference to these two, and scales constructed by means of which high temperatures can be measured by determining the light emitted from different incandescent substances. H. C.

Optical Measurement of High Temperatures. By H. Becquerel (*Compt. rend.*, **114**, 255—257) —Observations on a paper by Le Chatelier, dealing with the same subject (see preceding abstract). The author points out that the principle of the method recommended by Le Chatelier for the measurement of high temperatures is one which was put forward and fully explained by his father in 1862 (*Ann. Chim. Phys.* [3], **68**). H. C.

Specific Heat of the Diamond. By C. E. Carbonelli (*Gazzetta*, **22**, i, 123—130).—The author points out that the non-metallic elements in the seventh, sixth, and fifth groups of the Mendeléeff classification possess the general property of existing in the gaseous state in molecules containing two, three, and four atoms respectively. He considers that this periodicity may extend to the fourth group, which contains carbon, so that the gaseous molecules of elements in this group would contain five atoms. If this pentatomic molecule be supposed to preserve its individuality in the solid state the atomic heat of carbon must be multiplied by 5 to give the constant (6·4) of Dulong and Petit's law. The product of the specific heat of the diamond and the atomic weight of carbon is 1·25. On multiplying this by 5 a number (6·25) is obtained which accords with that required by Dulong and Petit's law. W. J. P.

Measurement of the Specific Heat of Liquids at Temperatures above their Boiling Points under Ordinary Pressure. By G. P. Grimaldi (*Real. Accad. Linc.*, **7**, ii, 58—63).—All the determinations of the specific heat of liquids at temperatures above

their boiling points under ordinary pressure have been hitherto made by the method of cooling, and the results obtained are very inconsistent. The author has devised an apparatus for making these measurements by the method of mixtures.

The liquid to be experimented on is contained in a steel cylinder A, whose sides are 3 mm. thick and whose volume is about 170 c.c. The cover communicates by means of a worm with another strong steel vessel B, in order to allow for the expansion of the liquid. When this whole arrangement has been raised to the required temperature in suitably heated jackets, the cylinder A is transferred to the calorimeter and the necessary thermometric measurements are made. The calorimeter, which has a capacity of about 5 litres, is made of very light polished brass, and contains petroleum, boiling above 300°, as the cooling liquid.

The specific heat of a cylinder of zinc is subsequently measured in the same apparatus, such a weight of metal being taken as to give approximately the same thermometric data as were obtained with the cylinder containing the liquid. From the two sets of measurements thus obtained, the specific heat of the liquid can be calculated. The results are satisfactory. W. J. P.

Heats of Combination of Bromine and Iodine with Magnesium. By N. Beketoff (*Chem. Centr.*, 1892, i, 11; from *Bull. Acad. St. Pétersbourg* [2], **34**, 291—292).—The author has determined the heats of solution of magnesium bromide and iodide. He takes Thomsen's determinations of the heat of combination of iodine and bromine with magnesium in solution; the difference being the heats of combination of the metal with the halogens. The results are: for magnesium bromide, 165000 − 43300 = 121700 cal., and for magnesium iodide, 134600 − 49800 = 84800 cal. Thus the combining heats of these halogens with magnesium are less than that of the oxide (140000 cal.) and the author suggests that it is another proof that the nearer the masses of two elements approximate to one another, the greater is the energy displayed in their combination. He prepared the anhydrous salts by means of Lerch's method—the direct combination of the halogen with excess of magnesium, in sealed tubes. J. W. L.

Heat of Formation of Potassium Tricarballylates. By G. Massol (*Compt. rend.*, **114**, 487—489).—The heat of solution of tricarballylic acid, melting at 163° (1 mol. in 6 litres of water) is −6·55 Cal. The heat of neutralisation with potash is +27·22, +24·94, and +19·58 Cal. for the first, second, and third acid radicles respectively (all substances calculated as solid).

Monopotassium tricarballylate, $C_6H_7O_6K + 2H_2O$, as obtained by evaporating the solution to dryness, is a hard, white, non-deliquescent mass. It loses the first molecule of water of crystallisation at 120°, and the second at 140°. *Dipotassium tricarballylate* crystallises in rhombic plates, and loses its water of crystallisation at 100.° *Tripotassium carballylate* is obtained in a similar way as a syrupy mass

which slowly thickens and solidifies when cooled. It loses its water of crystallisation at 130—135°. Jn. W.

Citric Acid. By G. Massol (*Compt. rend.*, **114**, 593—595).—The following thermal values were obtained with the sodium and potassium salts :—

	Potassium.	Sodium.
	Cal.	Cal.
Heat of neutralisation, MOH	+12·70	+12·65
„ „ 2MOH	+25·40	+25·52
„ „ 3MOH	+38·67	+38·40
$C_6H_8O_7$ sol. + MOH sol. = $C_6H_7O_7M$ sol. + H_2O sol.	+30·74	+26·59
$C_6H_7O_7M$ sol. + MOH „ = $C_6H_6O_7M_2$ „ + H_2O „	+25·32	+18·95
$C_6H_6O_7M_2$ „ + MOH „ = $C_6H_5O_7M_3$ „ + H_2O „	+17·63	+17·60
$C_6H_8O_7$ sol. + 3MOH „ = $C_6H_5O_7M_3$ „ + $3H_2O$ „	+73·69	+63·14
Heat of dissolution of the anhydrous salt, $C_6H_7O_7M$	− 7·97	− 6·35
„ „ „ „ $C_6H_6O_7M_2$	− 6·70	− 1·22
„ „ „ „ $C_6H_6O_7M_3$	+ 2·83	+ 5·27

The heats of neutralisation and of formation in the solid state are higher than the corresponding values of carballylic acid, the result being analogous to those obtained in the case of malonic and succinic acids and their hydroxy-derivatives. C. H. B.

Thermochemistry of the Carbohydrates and Polybasic Alcohols and Phenols. By F. Stohmann and H. Langbein (*J. pr. Chem.*, **45**, 305—356).—Continuing their work on the thermochemistry of food constituents and their derivatives (this vol., p. 4), the authors have determined the heats of combustion of a large number of carbohydrates and polybasic alcohols. The method employed was that described in former communications, and great care was taken to obtain the different substances dealt with in a state of purity. The results obtained are recorded in the following table, which contains in Columns I and II the heats of combustion per gram-molecule for constant volume and for constant pressure, and, in Column III, the heats of formation.

	I.	II.	III.
Pentoses :—	Cal.	Cal.	Cal.
Arabinose, $C_6H_{10}O_5$	558·3	558·3	256·7
Xylose, $C_6H_{10}O_5$	561·9	561·9	253·1
Rhamnose, $C_6H_{12}O_5$	718·2	718·5	259·5
Rhamnose, cryst., $C_6H_{12}O_5,H_2O$	711·5	711·8	335·2
Fucose, $C_6H_{12}O_5$	711·9	712·2	265·8
Hexoses :—			
d-Glucose, $C_6H_{12}O_6$	673·7	673·7	304·3
d-Fructose, $C_6H_{12}O_6$	675·9	675·9	302·1
Galactose, $C_6H_{12}O_6$	669·9	669·9	308·1
Sorbinose, $C_6H_{12}O_6$	668·6	668·6	309·4
Saccharin, $C_6H_{10}O_5$	656·9	656·9	252·1

	I.	II.	III.
Disaccharides:—			
Cane sugar, $C_{12}H_{22}O_{11}$	1352·7	1352·7	534·3
Milk sugar, $C_{12}H_{22}O_{11}$	1351·4	1351·4	535·6
Milk sugar, cryst., $C_{12}H_{22}O_{11},H_2O$	1345·2	1345·2	610·8
Maltose, $C_{12}H_{22}O_{11}$	1350·7	1350·7	536·3
Maltose, cryst., $C_{12}H_{22}O_{11},H_2O$	1339·8	1339·8	616·2
Trehalose, $C_{12}H_{22}O_{11}$	1349·9	1349·9	537·1
Trehalose, cryst., $C_{12}H_{22}O_{11},2H_2O$	1345·3	1345·3	679·7
Trisaccharides:—			
Melitose, $C_{18}H_{32}O_{16}$	2026·5	2026·5	769·5
Melitose, cryst., $C_{18}H_{32}O_{16},5H_2O$	2019·7	2019·7	1121·3
Melicitose, $C_{18}H_{34}O_{17}$	2043·0	2043·0	822·0
Polysaccharides:—			
Cellulose, $(C_6H_{10}O_5)x$	678·0	678·0	231·0
Starch, $(C_6H_{10}O_5)x$	677·5	677·5	231·5
Dextran, $(C_6H_{10}O_5)x$	666·2	666·2	212·8
Inulin, $C_{36}H_{62}O_{31}$	4092·1	4092·1	1230·9
Alcohols:—			
Ethylene glycol, $C_2H_6O_2$	281·4	281·7	113·3
Glycerol, $C_3H_8O_3$	396·8	397·1	160·9
Erythritol, $C_4H_{10}O_4$	504·1	504·4	216·6
Penterythritol, $C_5H_{12}O_4$	660·8	661·4	222·6
Arabitol, $C_5H_{12}O_5$	611·7	612·0	272·0
Mannitol, $C_6H_{14}O_6$	727·6	727·9	319·1
Dulcitol, $C_6H_{14}O_6$	723·6	723·9	323·1
Perseitol, $C_7H_{16}O_7$	835·8	836·1	373·9
Phenols:—			
Phenol, C_6H_6O	731·9	732·5	38·5
Catechol, $C_6H_6O_2$	684·9	685·2	85·8
Resorcinol, $C_6H_6O_2$	683·1	683·4	87·6
Quinol, $C_6H_6O_2$	683·0	683·3	87·7
Pyrogallol, $C_6H_6O_3$	639·0	639·0	132·0
Quercitol, $C_6H_{12}O_5$	704·1	704·4	273·6
Inositol, $C_6H_{12}O_6$	662·3	662·3	315·7

It will be noticed that the heats of combustion of many isomerides, such as arabinose and xylose, are very nearly identical, although this rule is not without several exceptions. Among the dihydroxybenzenes, the ortho- has the greatest and the para- the smallest heat of combustion, a fact which holds also for other benzene di-derivatives. It may be pointed out that a similar relation was observed by Ostwald to hold in the case of the affinity coefficients of these compounds. The combination of water of crystallisation with the different carbohydrates is, as an examination of the table will show, an exothermic process, and the same is true also of the action of hydrolytic agents in several cases which the authors examined. In the conversion of the sugars into the corresponding alcohols, also, heat is evolved, and it will be noticed that the difference between the heats of combustion of the alcohol and the sugar is in all cases

very nearly the same. A comparison of the heats of combustion of the alcohols with those of the hydrocarbons shows that the addition of each hydroxyl group in place of hydrogen in the hydrocarbon reduces the heat of combustion by about 44·7 cal., or that the heat of combustion of any alcohol will be $x44{\cdot}7$ cal. lower than that of the corresponding hydrocarbon. The constant varies from 39·5 to 47·0 cal. in different cases. H. C.

Theory of Heat of Solution and of Osmotic Pressure. By C. Dieterici (*Ann. Phys. Chem.* [2], **45**, 589—590).—An appendix to the author's paper under the same title (this vol., p. 676), in which he draws attention to some points connected with osmotic pressure raised by Lothar Meyer (*Sitz. Akad. Wiss. Berlin*, December, 1891). J. W.

Cryoscopic Communications. By J. Traube (*Ber.*, **25**, 1242—1243).—The author finds that in determining the freezing point of a liquid it is necessary that the temperature of the atmosphere in the surrounding space should not be more than 5° higher than the freezing point of the liquid, as, otherwise, the latter is found too high; thus, in a room at a temperature of 15—20° the freezing point of water was found, after 15 minutes, to be 0·03° higher than when first taken. The numbers previously given by the author for very dilute solutions, therefore, require a slight correction, which brings them more in accordance with those of Pickering. H. G. C.

Specific Gravities of Aqueous Solutions. By G. Charpy (*Compt. rend.*, **114**, 539—542).—In aqueous solutions of chlorides and sulphates, the sp. gr. corresponding to a given concentration is higher the greater the molecular weight of the salt, provided that the concentration is represented by the ratio of the number of molecules of the dissolved compound to the total number of molecules of the solution.

Increased sp. gr. of the solution with increased molecular weight is not general. In the case of the fatty acids, for instance, the sp. gr. diminishes as the molecular weight rises. Since there is always a contraction, if the sp. grs. of the two liquids are not widely different, there will be a particular degree of concentration showing a maximum sp. gr., and the solution showing the maximum will be weaker the greater the contraction, or, in other words, the higher the molecular weight of the acid. The existence of such a maximum in the case of acetic acid is well known; the author finds that the molecular concentration corresponding with this maximum is 55 in the case of acetic acid, 45 with propionic acid, 10 with butyric acid, and 1 with valeric acid.

The variation in the sp. gr. of a solution as a function of the concentration is a very complex phenomenon, and cannot be used in the investigation of the state of dissolved compounds as in the experiments of Pickering and of Mendeléeff.

Mixtures of methyl alcohol and amyl alcohol, and of benzene and ethyl acetate have sp. grs. which vary with absolute regularity as the concentration varies, and hence in these cases there is no contraction.

It follows that the contractions observed in the case of aqueous solutions are due either to a peculiar constitution of the water molecule or to the existence of a real chemical combination between the solvent and the dissolved substances. C. H. B.

Changes of Volume of Solutions of Salts. By Skubich (*Chem. Centr.*, 1892, i, 118—119; from *Apoth. Zeit.*, **6**, 662—663).—The author discusses the causes which occasion a change in volume when substances are dissolved in water: (1) the volume of a chemical compound is usually less than the sum of its components; (2) most salts occupy a less volume in solution than in the anhydrous state; (3) if a reduction in volume occurs in the preparation of a saturated solution of any salt, such a solution will dissolve a further quantity of the salt when subjected to increased pressure, whereas if the volume of the salt increase, pressure will cause a separation of salt from the solution saturated under the ordinary pressure. J. W. L.

Compressibility of Saline Solutions. By H. Gilbault (*Compt. rend.*, **114**, 209—211).—The method of experimenting was similar to that made use of by Cailletet in his researches on the compressibility of solutions, special precautions being taken to remove all traces of gas from the liquid and to maintain a constant temperature during each experiment. The observations were made at temperatures between 10° and 35°. For dilute solutions, the difference between the compressibility of water and that of the solution, or, as the author terms it, the saline compressibility, is proportional to the concentration whatever be the nature of the salt or the solvent. When a certain concentration is reached, the compressibility, increases less rapidly than the amount of salt dissolved, and if the behaviour of different salts throughout is represented in curve form, all the curves are, after suitable orientation, superposable. The compressibility of dilute solutions is affected more by change of temperature than that of concentrated solutions, and usually in the reverse manner, so that for each salt there generally exists a certain concentration for which the compressibility remains unaltered by change of temperature. If the same salt is dissolved in different solvents, the saline compressibilities will be in the same order as the compressibilities of the pure solvents, and the quotients of the saline compressibility divided by the compressibility of the solvent will be all the same. H. C.

Nature of Colloïd Solutions. By C. E. Linebarger (*Amer. J. Sci.* [3], **43**, 218—223).—Colloïd solutions differ from emulsions in their power of diffusion, emulsions not having the power of diffusion, but being subject only to the action of gravity. Diffusion, as has been shown by Nernst, is due to osmotic pressure, and a solution that diffuses should have an osmotic pressure. Osmotic pressure affords, as Van't Hoff has shown, a means of determining molecular mass, and determinations of the osmotic pressure of colloïd solutions should throw some light on the nature of the substances contained in such solutions.

The author determined the osmotic pressures of two solutions of

colloïd tungstic acid, one containing 0·02467 gram and the other 0·0100 gram of tungstic acid in 1 c.c. As a mean of the two determinations the molecular mass of colloïd tungstic acid was found to be about 1700, or nearly seven times 250, the number corresponding with the simple molecule H_2WO_4. The colloïd molecule would therefore consist of seven simple molecules in the case of tungstic acid, and this is in keeping with the ordinary assumption that the molecules of colloïds are very large.

A colloïd solution may be regarded as a step between a true solution and a true emulsion. The colloïd molecule is so much larger than the water molecule that it stands to reason that the properties of colloïd solutions must differ markedly from solutions of substances which have a molecule but several times heavier than water. Hence diffusion of colloïds takes place slowly; the osmotic pressure is small, and there is only a slight lowering of the freezing point or raising of the boiling point. H. C.

The Recognition of Changes of Curvature by means of a Flexible Lath. By S. U. Pickering (*Phil. Mag.*, **33**, 436—466.)—The author gives an exhaustive examination of four series of experiments which shows that the use of a flexible lath and of parabolas deduced from the experimental values leads to the same conclusions as to the existence and position of any changes of curvature. He first obtains a method for estimating the error of a drawing; the mean apparent error of the points, the number of points represented as showing excessive errors, and the arrangements of errors with like signs into groups are the three factors taken as constituting the total error of the drawing, and this error should be very nearly identical with the ascertained experimental error, if the drawing is to be acceptable. In all the cases investigated, this is so when the drawing represents the existence of the breaks in question, whereas a drawing or parabola which obliterates them exhibits an error many hundred and even thousand times greater than the experimental error. On the other hand, the introduction of fictitious breaks into a curve which is really continuous produces little or no reduction in the total error, and such a drawing can, therefore, not be accepted as "the simplest interpretation which is in harmony with the experimental error."

In the case of well-marked breaks, their position cannot be shifted even a short distance without increasing the apparent error beyond legitimate limits. Neither the position nor the existence of these breaks are subject to the "taste" of the draughtsman. In the case of a true break, it will appear consistently whatever form of plotting be adopted; six instances are given. The author also found that in a case where two parabolas, showing a break, and containing together seven constants, represented the results perfectly, a single parabola obliterating the break, but with the same number of constants, exhibited an error 25 times greater than the experimental error.

The author adds a few words in answer to some additional remarks of Rücker's on his interpretation of the densities of sulphuric acid.

S. U. P.

Velocity of Decomposition of Diazo-Compounds by Water. By P. T. Muller and J. Hausser (*Compt. rend.*, **114**, 549—552, 669—671 and 760—763).—Diazo-compounds dissolved in water decompose with evolution of nitrogen and formation of the corresponding phenol. The reaction takes place slowly at the ordinary temperature, and more rapidly as the temperature is raised. If a convenient temperature is chosen, it is possible to measure the velocity of the reaction by measuring the volume of nitrogen liberated in a given time.

The authors find that the decomposition of 1 : 4-diazobenzenesulphonic acid obeys the ordinary laws of mass action, and takes place in accordance with the equation $dx/d\theta = C(A - x)$, where x represents the amount of nitrogen liberated in the time θ, and A the total amount of nitrogen present. The constant C is independent of the concentration. The decomposition of the 1 : 3-acid does not take place in quite so simple a manner, but may be expressed by the equation $dx/d\theta = (A - x)(C + 2k\theta)$. The constant C varies with the concentration. The decomposition of the meta-acid is also far more rapid than that of the para-acid. Diazotoluenesulphonic acid (Me : SO_3 : N_2 = 1 : 2 : 4) behaves like the paradiazobenzenesulphonic acid, but the behaviour of paradiazotoluene sulphate is like that of the meta-acid. The exceptional behaviour of the two latter compounds is supposed to be due to the influence of the phenol produced in each case. The experiments were made at 64°. H. C.

Flameless Incandescence produced by Coal Gas. By F. Parmentier (*Compt. rend.*, **114**, 744—746).—The author has investigated some of the conditions affecting the well known phenomenon of incandescence produced when a mixture of coal gas and air such as proceeds from an unlighted Bunsen burner is allowed to impinge upon warm platinum. With platinum wire, the incandescence is more intense, and the ignition of the gaseous mixture is more readily produced, the thinner the wire and the brighter and cleaner its surface. The difference is doubtless due to the smaller loss of heat by conduction when the wire is thin, and the smaller loss of heat by radiation when the surface is bright.

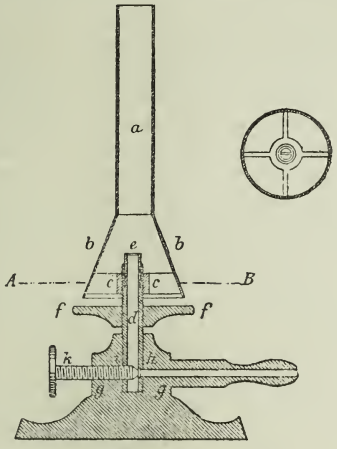
If platinum wire gauze is used, a ring of it concentric with the axis of the burner rapidly rises to a red heat, the gas above the gauze next takes fire, and afterwards the gas below the gauze ignites also.

Under similar conditions, spongy platinum becomes dull red, but the gaseous mixture is not ignited.

Platinum crucibles become hotter, and ignite the gaseous mixture more frequently the smaller they are and the brighter their surface. The larger the surface in proportion to the mass in the case of crucibles, dishes, &c., the lower the temperature to which the metal rises. Generally, any cause which tends to increase the loss of heat by conduction, radiation, convection currents of air, &c., reduces the temperature to which the metal is raised, and makes ignition of the gaseous mixture less frequent. C. H. B.

New Laboratory Burner. By N. Teclu (*J. pr. Chem.* [2], **45**, 281—286).—In summing up the points of an effective burner of the

Bunsen type, the author insists on the necessity for (1) a tube which shall be wide enough to admit of the influx of sufficient air, but not wide enough to diminish the pace of the stream of gas; (2) a tube long enough to ensure sufficient time for the complete mixture of the air drawn in with the gas; (3) the substitution of a screw-cock for the usual gas-cock; (4) an air inlet which shall have as large a surface as possible, and be concentric with the ascending column of gas. It is claimed that the burner here depicted combines these qualities, and can be used either as an ordinary Bunsen burner or a "solid flame" burner by regulating the air supply.



The combustion tube *a* is 10 cm. long and 10 mm. in diameter; the mouth of the funnel-shaped portion *b* is 2·5 cm. in diameter; the section of the funnel represented at AB will serve to explain how the tube is fixed on to the gas jet *d* by means of the screw *cc*. The regulating plate *f* is 3 cm. in diameter, and can be screwed up and down on the tube *d*. The screw *k* serves to regulate the gas supply. The gas jet *e* is 4 mm. long and 0·5 mm. wide, and is 2 cm. up the combustion tube. The tube by which the gas enters is 3·5 mm. in diameter. A. G. B.

Inorganic Chemistry.

Solubility of Iodine in Chloroform. By W. Duncan (*Pharm. J. Trans.*, **51**, 544).—Although the statements in the books imply that iodine is freely soluble in chloroform, the author finds that at 10°, 1 part of the iodine requires for solution as much as 56·6 parts of chloroform. R. R.

Action of Sulphur on Metallic Solutions. By J. B. Senderens (*Bull. Soc. Chim.* [3], **6**, 800—807).—Oxides of the alkalis and alkaline earths, when boiled with sulphur and water, react according to the equation:—

$$3M'O + nS + xH_2O = 2M'S_{n-2} + M'S_2O_3 + xH_2O,$$

when the solutions are concentrated; with weaker solutions, a greater amount of thiosulphate is formed from the decomposition of polysulphides, and hydrogen sulphide is liberated; but, under the most favourable conditions, not more than half of the alkaline polysulphides is so converted, even after prolonged boiling. When sulphur is triturated with mercurous oxide, the mixture inflames, and sulphurous anhydride with mercuric sulphate and sulphide are formed; with chromic anhydride, it behaves similarly, and the residue, treated with water, affords chromic chromate and chromic sulphate, although an aqueous solution of the anhydride is hardly affected by sulphur.

Silver oxide and carbonate are slowly decomposed by sulphur in presence of water at the normal temperature, and at 100° the action is complete: silver sulphate being formed, which subsequently decomposes into silver sulphide and hydrogen sulphate; the corresponding cuprous and cupric compounds also suffer decomposition when so treated, cupric sulphide being produced in each case. On boiling the oxides and hydroxides of mercury, lead, bismuth, cadmium, nickel, and cobalt with sulphur in water, their sulphides and sulphates are obtained, the cobalt reacting less readily than the nickel compounds, and yielding in addition some thiosulphate. Manganese and magnesium hydroxides afford their sulphides and thiosulphates, the compound MgS_3 being formed in the latter case.

The oxides of iron, zinc, and tin are not affected by this treatment, neither are the sulphates, nitrates, and chlorides of the alkalis, the alkaline earths, and of nickel, cobalt, cadmium, lead, and mercury; but the corresponding salts of silver and copper are slowly decomposed in the cold, and rapidly on boiling, with formation of argentic and cupric sulphides.

Solutions of acetates of the alkalis and alkaline earths are decomposed on boiling with sulphur; hydrogen sulphide, and acetic acid are liberated, and a thiosulphate is formed, while alkaline carbonate and bicarbonate solutions are decomposed below 100° with evolution of carbonic anhydride and hydrogen sulphide and formation of a thiosulphate.

Sulphur reduces boiling potassium chromate solution; hydrogen sulphide is given off, chromium sesquioxide is precipitated, and potassium thiosulphate is formed. Potassium dichromate solution affords, in like manner, chromium chromate with potassium sulphite and sulphate; argentic and mercuric chromates are also attacked, but the lead salt is unaffected.

Sulphur decomposes boiling solutions of sodium and calcium silicate with formation of polysulphides, of some thiosulphate, and evolution of hydrogen sulphide, while sulphur, boiled with powdered glass, determines a similar reaction which is prevented by a previous addition of hydrochloric acid.

The author is unable to confirm the statement that sulphur and water react at 100° to form hydrogen sulphide and sulphurous anhydride, and he considers the evolution of hydrogen sulphide, under such circumstances, to be due to the action of the sulphur on the glass vessels used. T. G. N.

Preparation of Crystallised Hydroxylamine. By L. Crismer (*Bull. Soc. Chim.* [3], **6**, 793; compare Abstr., 1890, 558).—A mixture of dry hydroxylamine zinc chloride (10 grams), and anhydrous aniline (20 c c.), is distilled under a pressure of 20 mm. on a water-bath. The distillate of hydroxylamine, which crystallises on cooling, is washed with ether, care being taken to prevent access of moist air. Or dry ammonia gas is passed through absolute ether holding the zinc salt in suspension, and the decanted ethereal solution of hydroxylamine is subsequently distilled under reduced pressure, when crystals are obtained. The author confirms Lobry de Bruyn's observations on the crystals (this vol., p. 402). T. G. N.

Combination of Ammonia with Boron Bromide and Iodide. By A. Besson (*Compt. rend.*, **114**, 542—544).—Ammonia gas combines directly with boron bromide with great development of heat and partial conversion into boron nitride. In order to obtain a definite compound, all rise of temperature must be avoided. If dry ammonia, cooled to 0°, is passed into a solution of boron bromide in dry carbon tetrachloride, cooled to 0°, a white, solid substance separates, and at the end of the reaction the solvent is expelled by means of a current of dry air at 50—60°. The product is amorphous, and has the composition $BBr_3,4NH_3$. At 10° it absorbs more ammonia, but the excess is expelled in a current of dry air. When heated in dry hydrogen, decomposition begins at about 150°, without sublimation, the products being boron nitride and ammonium bromide. The compound is also decomposed by water and alkalis.

Boron iodide, under similar conditions, yields a white, amorphous compound, $BI_3,5NH_3$, which becomes brown when exposed to light, a small quantity of iodine being liberated. It is also decomposed when heated in a current of hydrogen, iodine being liberated, and it is decomposed by water. In a current of dry ammonia, the compound $BI_3,5NH_3$ absorbs the gas rapidly, and yields a liquid approximately of the composition $BI_3,15NH_3$; but even at 0° this compound is unstable, and in a current of dry air it gradually loses ammonia, and is reconverted into the original compound.

Boron iodide forms a crystalline compound with hydrogen phosphide.

In the preparation of boron iodide by the action of hydrogen iodide on amorphous boron obtained by the method of Deville and Wöhler, only a small portion of the boron is attacked, and this portion seems to be a more active variety than the remainder of the boron.

C. H. B.

Carbon Chlorobromides. By A. Besson (*Compt. rend.*, **114**, 222—224).—Bromine and chloroform in molecular proportion are heated in strong, sealed tubes for two hours at 225°; on opening the

tubes, a gas is given off consisting chiefly of hydrogen bromide; the heating is continued for some hours at 250°, after which the gas disengaged is mostly hydrogen chloride; the reaction terminates at 275°.

The three chlorobromides indicated by theory are thus obtained and can be separated by fractionation. The chlorobromide CCl_3Br fuses at −21°. The substance CCl_2Br_2 crystallises in fine needles melting at 22°; it distils at about 135°; its density at 25° is 2·42. Its odour resembles that of chloroform; it volatilises very rapidly at the ordinary temperature, and its vapour tension is 21 mm. at 16°, 31 mm. at 30°, and 268 mm. at 100°.

The chlorobromide $CClBr_3$ crystallises from its ethereal solution in transparent plates which melt at 55°; it distils at 160° with slight decomposition. It has the consistency of wax when melted; its odour recalls that of carbon tetrabromide. It is very soluble in ether, chloroform, carbon tetrachloride, carbon bisulphide, and benzene, less soluble in alcohol. Its density at 15° is 2·71. Attempts to obtain this substance as a brominated derivative of methyl chloride have failed.

The compound $CHBr_2Cl$ is easily obtained, but when this is heated with bromine at 250°, it yields bromoform and carbon tetrabromide; by carrying out the reaction at 200—225°, crystals have been obtained melting at 75°, and apparently consisting of a mixture of the compounds $CClBr_3$ and CBr_4, which are probably isomorphous, and have not been completely separated. W. T.

Action of Ammonium Chloride at its Dissociation Temperature on Silicates. By E. A. Schneider and F. W. Clarke (*Ber.*, **25**, 883—886).—In the course of a research on the constitution of natural silicates (Abstr., 1891, 529, and this vol., p. 125), the authors specially examined the action of dry hydrogen chloride on these compounds. For the sake of convenience, they now employ ammonium chloride. The following is the method of working:—A mixture of the finely-powdered silicate (1 gram) and dry ammonium chloride (10 grams) is heated in a platinum crucible at the temperature at which the ammonium chloride is rapidly volatilised, but below the dehydration temperature of the silicate. When all the ammonium chloride is volatilised, the residue in the crucible is extracted with water and the solution analysed. In some cases the residue is treated two or three times with ammonium chloride before extracting with water.

Olivine and xanthophyllite var. waluewite are scarcely attacked by ammonium chloride or by dry hydrogen chloride, although easily decomposed by the aqueous acid. On the other hand, the action on serpentine, klinochlor, and leuchtenbergite is considerable. The above silicates contain magnesia as a chief constituent. The silicates of the latter group probably contain the radicle –Mg·OH; whilst those of the first group do not. This reaction may possibly be used to determine the presence of the group –Mg·OH.

Of silicates which do not contain magnesia: natrolite,

$$Al_2Si_3O_{12}Na_2H_4,$$

after treatment three times with ammonium chloride, yielded 9·5 per cent. of sodium oxide as sodium chloride; prehnite, $Al_2Si_3O_{12}Ca_2H_2$, gave only 1·72 per cent. of calcium oxide as chloride; wollastonite, $CaSiO_3$, and pectolite, $Ca_2NaHSi_3O_9$, are attacked energetically by ammonium chloride, and gave respectively 36·98 per cent. CaO and 20·5 per cent. CaO, 6·95 per cent. Na_2O, and 0·54 per cent. MnO as chlorides. Here the action of dry hydrogen chloride is not dependent on the presence or absence of hydroxyl groups in these silicates.

The authors have also examined the action of ammonium chloride on various phosphates. Lazulite and turquoise are scarcely attacked; dufrenite is attacked energetically, and a considerable quantity of ferric chloride is formed. E. C. R.

Definite Alloys of Sodium. By Joannis (*Compt. rend.*, **114**, 585—587).—The author has previously shown that when an excess of lead is brought in contact with sodammonium, a compound

$$Pb_4Na,2NH_3$$

is obtained (this vol., p. 275). When the sodammonium is in excess, and the product is repeatedly washed with liquefied ammonia until excess of sodium is removed, the residue is a mixture of sodium amide, NH_2Na, and a perfectly definite alloy, PbNa. The alloy is readily obtained pure by the action of liquefied ammonia on a mixture of lead and sodium in atomic proportions. It is decomposed by water with formation of sodium hydroxide and liberation of lead in black flakes. When exposed to air, it rapidly becomes hot.

The potassium alloy is formed under similar conditions, and is more easily obtained in consequence of the greater solubility of potassium amide in liquefied ammonia. It has the composition Pb_2K.

An alloy of sodium and bismuth, $BiNa_3$, is obtained by the action of sodammonium in excess on pure bismuth. It forms a bluish-black granular mass, takes fire when exposed to air, and is decomposed by water with evolution of practically pure hydrogen. The analogy between the composition of this alloy and that of ammonia, phosphine, and hydrogen arsenide is of considerable interest.

An alloy of sodium and antimony, $SbNa_3$, is obtained in a similar manner. It oxidises very easily, takes fire when exposed to air, and is decomposed by water with evolution of pure hydrogen.

C. H. B.

Salts of Cæsium containing 3 Atoms of Halogen to 1 of Metal. By H. L. Wells and S. L. Penfield (*Amer. J. Sci.*, **43**, 17—32; compare Remsen, this vol., p. 779).—The compounds CsI_3, $CsBrI_2$, $CsBr_2I$, $CsClBrI$, $CsCl_2I$, $CsBr_3$, $CsClBr_2$, and $CsCl_2Br$ are obtained on dissolving, with the aid of heat, the appropriate normal cæsium halogen salt, and the halogen or halogens indicated by the formulæ, in a convenient quantity of water, or, in the single case of $CsBrI_2$, in dilute alcohol, and cooling until crystallisation occurs. The five compounds containing iodine are much more stable than the others, and will bear long exposure to the air at the ordinary temperature, but with very slight superficial change.

The three compounds containing no iodine usually become white on exposure for a few hours; but the stability of the compounds does not entirely depend on the volatility of the halogens contained in them. All the compounds except $CsBrI_2$ can be recrystallised from alcohol or from a mixture of alcohol and water. They form isomorphous, orthorhombic crystals, and a very remarkable relation exists between those containing iodine, the ratio of the two axes remaining nearly constant throughout, whilst the third varies. Exactly the same relations exist between the compounds containing no iodine, but in this series the ratio between the two constant axes varies slightly from the corresponding ratio in the iodine compounds. If an arrangement according to molecular weights is made with all the compounds containing bromine, or in a like manner with all those containing chlorine, a symmetrical series of axial ratios is not formed. This leads to the conclusion that the two series indicated have a special significance, and that iodine, with the highest atomic weight, plays an important part in the constitution of the first, whilst bromine acts in the same way in the second. Since several of the compounds contain only a single halogen atom of highest atomic weight, it follows that a single atom throughout exerts an influence on the symmetry of the series. This peculiar part, played by an iodine or bromine atom, may be explained by supposing it to be closely united either with cæsium or with one of the other halogen atoms. It seems probable from these considerations that the three halogen atoms in the compounds do not occupy similar positions in the molecules, and consequently that the salts described are not compounds of trivalent cæsium, but have some other structure.

The following table gives the chief properties of the compounds, which are well characterised:—

	Colour.	Melts in open tube.	Melts in closed tube.	Completely decomposes.
Series with iodine—				
CsI_3	Brilliant black	210°	201—208°	330°
$CsBrI_2$	Dark reddish-brown..	208	155—190	260
$CsBr_2I$	Deep cherry-red.....	246	243—248	320
$CsClBrI$	Dark yellowish-red ..	238	225—235	290
$CsCl_2I$	Deep or pale orange..	238	225—230	290
Series without iodine—				
$CsBr_3$	Yellowish-red.....	whitens	180°	160
$CsClBr_2$	Pale yellowish-red ...	whitens	191	150
$CsCl_2Br$	Bright yellow.....	whitens	205	150

Attempts to prepare the other two possible salts, $CsClI_2$ and $CsCl_3$, were unsuccessful.

The crystallographic properties of the compounds above described harmonise with the view advanced by Remsen (*loc. cit.*) to explain the composition of double halogen salts, namely, that two halogen atoms can behave as bivalent oxygen. G. T. M.

Organosols. By E. A. Schneider (*Ber.*, **25**, 1164—1167).—The author applies the term "organosol" to the solution of a colloïd in an organic liquid, he also adds the formula of the colloïd and, in brackets, the name of the solvent.

Organosol Au_2S_2 (ethyl alcohol) is prepared by mixing an aqueous solution of aurosoauric sulphide (1·514 grams per litre) with 3 vols. of absolute alcohol, and dialysing this solution in absolute alcohol; the organosol closely resembles the hydrosol, but is more stable.

Organosol Au_2S (ethyl alcohol) is obtained in a manner similar to the preceding, but the solution, which is straw-coloured, only contains 0·001 per cent. Au_2S.

Organosol Ag (ethyl alcohol) is formed by the dialysis of the hydrosol in absolute alcohol, or by adding alcohol to the hydrosol, allowing it to coagulate, filtering by means of a Pasteur's tube, and dissolving the silver in absolute alcohol. A solution containing 0·1746 per cent. Ag is opaque, in layers of 2 mm. in thickness; on dilution, the colour is greenish-blue and finally yellowish-green in transmitted light, and violet-brown in reflected light. On distilling off the alcohol, the silver is deposited as a golden-yellow mirror.

The author suggests that it may be possible to explain the variations in colour of silver solutions by known optical laws without assuming the existence of allotropic modifications. J. B. T.

Preparation of Pure Colloïdal Silver. By E. A. Schneider (*Ber.*, **25**, 1281—1284).—Solutions of ferrous sulphate (150 grams of the salt in 500 c.c. of the solution) and of sodium citrate (280 grams of the salt in 700 c.c. of the solution) are mixed, and poured into a 10 per cent. solution of silver nitrate (500 c.c.). Day-light need not be excluded, but it is advisable to divide the mixture into five equal portions, as small quantities can be dealt with more easily than large. At the end of half an hour the supernatant liquid is removed from the precipitated colloïdal silver with a pipette, and the silver is thrown on to a filter (Schleicher and Schüll's No. 590 paper), filtered under diminished pressure, and dissolved on the filter in the minimum quantity of water; solutions may be thus obtained containing 20 grams of silver per litre. To this solution absolute alcohol is added with agitation until coagulation is perceptible, and, after remaining for several days, the colloïd is filtered under a diminished pressure of 10—20 mm. on a Pasteur filter-tube, when it forms a beautiful, iridescent incrustation. Colloïdal silver in this state of purity is soluble in alcohol, and cannot, therefore, be washed with this liquid to remove the last traces of crystalloïds. By this method, a product containing only 0·3—0·5 per cent. of iron salts is obtained.

A. R. L.

Action of Light on Silver Chloride. By A. Béchamp (*Bull. Soc. Chim.* [3], **6**, 836—840).—The author investigated the action of light on silver chloride under water in 1853, and found that after four days' exposure the silver chloride lost nearly 2 per cent. by weight, whilst the water precipitated silver nitrate and decolorised indigo. On fusing the altered silver chloride, it formed a lower horny, yellow,

transparent layer and an upper black, porous mass. (Compare Abstr., 1891, 1420.) T. G. N.

Separation of Barium from Strontium Salts. By Adrian and Bougarel (*J. Pharm.*, **25**, 345—348). If to a solution of a strontium salt containing barium there is added an excess of precipitated calcium sulphate, after a few hours' contact, with occasional stirring, the barium is completely removed from solution. Calcium is substituted for the barium, but can be removed by a couple of crystallisations. On these data, the authors found a commercial process commencing with commercial strontium carbonate or hydroxide, nitric acid, sodium carbonate, and calcium sulphate, and producing pure strontium carbonate, from which other pure strontium salts can be obtained, and commercial sodium nitrate. The process is equally applicable to strontium chloride, acetate, &c. J. T.

Nitrides of Barium and Strontium. By Maquenne (*Compt. rend.*, **114**, 220—222).—A current of nitrogen is passed, at a red heat, over an electrolytic amalgam of barium or strontium contained in an iron or nickel boat, when a product is obtained consisting of barium or strontium nitride, excess of the corresponding metal, finely divided iron or nickel from the boat, a little mercury, and a trace of baryta or strontia formed during the manipulation of the amalgam.

The quantity of hydrogen liberated on treating the mass with water is very variable; it is evidently derived from the action of water on the free barium or strontium present.

Correcting for the impurities found, barium nitride gives from 5·59 to 5·97 per cent. of nitrogen, and strontium nitride similarly gives 9·96 per cent. The formulæ N_2Ba_3 and N_2Sr_3 require 6·38 and 9·64 per cent. respectively.

Barium nitride does not give ethyl bases with alcohol. At a red heat, it reacts energetically with carbonic oxide, with production of baryta and barium cyanide.

Strontium nitride, under similar conditions, gives but a trace of cyanide.

This property of barium nitride explains the synthesis of barium cyanide from nitrogen, carbon, and baryta at a red heat. W. T.

Action of Magnesium on Chlorides. By K. Seubert and A. Schmidt (*Annalen*, **267**, 218—248).—The authors have studied the action of magnesium at various temperatures on the chlorides of a large number of elements; in some cases neutral, acid, and ammoniacal aqueous solutions of the chlorides, containing about 1 per cent. of the metal, were employed; in others the anhydrous chloride was used, and under these conditions a very violent reaction generally took place. It was noticed that, in some cases, the reduction of acid aqueous solutions of chlorides is not so effectively accomplished when the magnesium is employed in the form of filings as when it is used in the shape of small blocks or cubes.

The following is a summary of the results of the investigation:—

Family I: *Group* A.—Aqueous solutions of the chlorides of the

alkalis are not acted on by magnesium under any conditions; at a red heat, especially in an atmosphere of hydrogen, the chlorides are reduced to the corresponding metal, lithium being more readily acted on than sodium chloride, and the latter more readily than potassium chloride. *Group* B.—From neutral aqueous solutions of cupric chloride cuprous oxide is precipitated, from acid solutions copper is precipitated, and from ammoniacal solutions copper is precipitated, whilst cuprous chloride remains in solution; the anhydrous chloride is reduced to metal. The chlorides of silver and gold are readily reduced to metal, both in the dry and in the wet way.

Family II: *Group* A.—The chlorides of calcium, strontium, and barium are not decomposed by magnesium in aqueous solution; at a red heat, and in a stream of hydrogen, they are reduced to the corresponding metal, and the more readily the lower the atomic weight of the metal. *Group* B.—The chlorides of zinc and cadmium give in neutral solution both the metal and the hydroxide, but from acid solutions only the metal is precipitated; in ammoniacal solution, zinc chloride gives both the metal and the hydroxide, but cadmium chloride yields only the metal. Mercuric chloride, in neutral and in acid solution, is first reduced to mercurous chloride and then to the metal. When the anhydrous chlorides are heated with magnesium, they are reduced to the corresponding metals.

Family III: *Group* A.—Anhydrous boron chloride is reduced to boron, with formation of magnesium boride. Aluminium chloride is not acted on in acid solution, but in neutral solution the hydroxide is precipitated; at a red heat it is reduced to metal. *Group* B.—Thallious chloride is reduced to metal both in the dry and in the wet way.

Family IV: *Group* A.—The chlorides of carbon and of silicon are reduced to the corresponding elements, but titanium chloride seems to be converted into the sesquichloride. *Group* B.—From a neutral solution of stannic chloride, stannic acid is precipitated, but both the chlorides of tin are reduced to metal in acid solution. Lead chloride invariably gives the metal.

Family V.—The chlorides of phosphorus, arsenic, antimony, and bismuth are reduced to the corresponding element at a red heat; in acid solution, the chlorides of arsenic and antimony give the corresponding element, and also its hydroxide, but bismuth chloride gives only the metal.

Family VI: *Group* A.—From a neutral solution of chromium chloride the corresponding hydroxide is precipitated, but no reaction occurs in acid solution. The anhydrous chlorides of chromium, molybdenum, tungsten, and uranium are reduced to the corresponding elements at a red heat. *Group* B.—Chloride of sulphur yields sulphur when it is heated with magnesium.

Family VII: *Group* A.—In neutral, and in ammoniacal solution, manganese chloride is converted into manganous hydroxide, but no reaction takes place in acid solution; at a red heat, the anhydrous chloride is reduced to metal.

Family VIII.—From neutral solutions of the chlorides of iron, cobalt, and nickel the lower hydroxides are precipitated; the chlorides of cobalt and nickel show the same behaviour in ammoniacal solution.

Acid solutions of iron and cobalt chloride are reduced to the corresponding metal, but nickel chloride is not acted on. Platinic chloride is always reduced to metal. All the chlorides of this group are reduced at a red heat.

Magnesium can be advantageously employed instead of zinc for the precipitation of antimony and tin from solutions of their chlorides; reduction takes place more quickly than when zinc is used, and no contamination with lead is to be feared. The great purity of magnesium prepared electrolytically and its more rapid action render it very suitable for various other purposes for which zinc is usually employed; as, for example, for the reduction of ferric to ferrous salts in the estimation of iron volumetrically. F. S. K.

Cadmium Sulphides. By G. Buchner (*Chem. Zeit.*, **15**, 329—331).—The author has made several practical experiments with the various modifications of cadmium sulphide. The α-sulphide: A heavy precipitate produced by hydrogen sulphide in neutral, or faintly acid, cadmium solutions. It has a very bright, lemon-yellow colour, and makes a good covering paint. Mixed with white, the colour becomes pure yellow, but never reddish. Its sp. gr. varies from 3·906 to 4·147. It probably crystallises in the same form as greenockite (native cadmium sulphide). Strong heating or rubbing, or treatment with zinc chloride, or nascent hydrogen changes it into the β-modification, whilst fusion with sulphur makes it pass into the δ-state.

Exposed to the influence of light and air, the compound is slowly oxidised to cadmium sulphate, but when made into paint the colour is very permanent. On heating, the sulphide gradually becomes deep-yellow, orange, carmine-red, and finally dark violet-red, but on cooling it slowly regains its original colour, unless the heat has been too strong and partial oxidation to cadmium oxide has taken place.

The β-sulphide: A heavy precipitate produced by hydrogen sulphide in strongly acid solutions. Its colour is very bright, and not unlike red lead. It makes a good covering paint and, when mixed with white, produces a reddish colour. Its sp. gr. is greater than the yellow variety, and varies from 4·492 to 4·513. When heated with acids, it changes into the α- form, before dissolving. Prolonged heating also has that effect. When perfectly free from any α- admixture, it is not oxidised either in the dry or moist state, by the combined influence of light and air. When made into paint, its colour is absolutely permanent, even in strong daylight.

Cadmium sulphide obtained, say, during an analysis, is very often a mixture of the α- and β-modifications. For practical painting purposes, these, or their mixtures are, according to the author, the only admissible ones.

The γ- or soluble sulphide: Colloïdal cadmium sulphide is formed by treating a solution of cadmium iodide with hydrogen sulphide. The liquid becomes deep-yellow without giving a precipitate, which, however, immediately forms on the addition of an acid or even of ammonium chloride.

The same sulphide is also produced when freshly precipitated and washed δ-sulphide is suspended in water and treated with hydrogen

sulphide. The sulphide slowly dissolves, and does not readily re-precipitate, even on boiling. The addition of alum or potassium sulphate causes the sulphide to precipitate as the δ-modification.

The δ-sulphide: A bulky, yellow precipitate produced by treating an ammoniacal solution of cadmium hydroxide with hydrogen sulphide. After being dried, it forms amorphous, resinous lumps of a dark, reddish-brown colour. L. DE K.

Double Halogen Salts. By I. REMSEN (*Amer. Chem. J.*, **14**, 81—89; compare Abstr., 1889, 934).—A further investigation of the double halogen salts of several metals (see next abstract, and pp. 780, 784, 788) confirms the law that "when a halogen salt of any element combines with a halogen salt of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to 1 mol. of the other halogen salt is never greater, and is generally less, than the number of halogen atoms contained in the latter." To this law, which is in accordance with the hypothesis of the double halogen atom acting as a bivalent group, there are but few exceptions; in fact, only three or four out of over 400 cases; and the author explains these by suggesting that three halogen atoms, in which each halogen atom is trivalent, may possibly form together a trivalent group. Such an assumption makes it possible to regard the double halogen salts as constituted similarly to other compounds, and removes the need of classifying them amongst the so-called molecular compounds. G. T. M.

Double Halogen Salts of Lead. By C. H. HERTY (*Amer. Chem. J.*, **14**, 107—126; compare preceding abstract).—The author finds that of the five double iodides of lead and potassium, PbI_2,KI, $PbI_2,4KI$, $PbI_1,2KI + 4H_2O$, $PbI_2,2KI + 2H_2O$, and $3PbI_2, 4KI + 6H_2O$, described by Boullay, Ditte, and Berthelot, only one exists. This is the salt $KPbI_3,2H_2O$, which loses its water of crystallisation at 110°, and is decomposed, with evolution of iodine, at 310°. The corresponding sodium salt, $NaPbI_3$, crystallises in small needles, and is very deliquescent.

The double bromide of lead and potassium, $KPbBr_3 + H_2O$, crystallises in large, colourless plates; but the corresponding sodium compound could not be separated. The double chloride of lead and potassium, $KPbCl_3$, crystallises in slender, white needles which are anhydrous; the double chloride of lead and sodium does not appear to exist.

All the salts described are decomposed by water, and, in order that they may exist in solution, a certain minimum amount of alkali halogen salt must be present, this amount varying inversely as the atomic weight of the halogen atom present in the compound. The quantity of the halogen salt of lead dissolved by the alkali halogen salt increases with the atomic weight of the halogen. Only a very small quantity of lead fluoride dissolves in a solution of potassium fluoride, a larger quantity of lead chloride in potassium chloride solution, a still larger quantity of lead bromide in potassium bromide solution, and, greatest of all, lead iodide in potassium iodide solution. On the other hand, the number of molecules of water of crystallisa-

tion contained in the double halogen salts decreases with the atomic weight of the halogens, thus: $KPbI_3 + 2H_3O$, $KPbBr_3 + H_2O$, and $KPbCl_3$.

All the double halogen salts of lead and the alkalis admit of their constitution being expressed by formulæ in which two halogen atoms play the part of the so-called linking oxygen atom, and are consequently in harmony with Remsen's law of combination of alkali halogen salts with the halogen salts of other metals. G. T. M.

Mercurous Hypochlorsulphite. By J. E. Gilpin (*Amer. Chem. J.*, **14**, 182—184; compare Remsen, this vol. p. 779).—In connection with the work on double halogen salts, it was considered important to ascertain the molecular weight of one of them by determining the specific gravity of its vapour. To this end the compound SCl_2,Hg_2Cl_2, described by Capitaine (*J. pr. Chem.*, **18**, 422), was employed; but it was found to dissociate on heating, its constituents recombining when the temperature was lowered. G. T. M.

Samarium. By L. de Boisbaudran (*Compt. rend.*, **114**, 575—577), —The author has previously described three lines, λ 466·2, λ 462·7. and λ 459·3, seen when the spark from a coil with a long wire is allowed to play on the surface of solutions containing samarium, and also a band at λ 611—622, seen when the current is reversed.

Some pure samarium, prepared by Cleve, was fractionated with ammonia. The three lines are no longer visible in the tail fractions, are feeble in the middle, but somewhat stronger in the head fractions. The band 611—622 is strongest in the head fractions, but is still visible in the tail; even at the head it is less brilliant than the orange band of samarium. Like the bands of $Z\beta$, the band 611—622 gains in brilliancy when the spark impinges on the centre of the liquid instead of at the side, whilst the orange band becomes somewhat less brilliant. Ferric chloride reduces the intensity of the orange band, but has still more effect on the band 611—622.

The three well known bands of samarium show marked differences in intensity when the point of impact of the spark on the liquid is altered. It is possible that there is a relation between the band 611—622 and the narrow band observed by Crookes in mixtures of basic yttrium and samarium sulphates. The author has observed the same, or an analogous, ray with many products; its position varies distinctly with the nature of the solid solvent employed. It is accompanied by a feebler and more refrangible ray. Lanthanum sulphate, with a little samariferous gadolinite, shows the stronger ray at 612·7, and the weaker at 619·6. Crookes gives 609 for his ray, but the difference in position may be due to the difference in the nature of the solvent. C. H. B.

Double Halogen Salts of Manganese. By C. E. Saunders (*Amer. Chem. J.*, **14**, 127—151; compare Remsen, this vol., p. 779). —In attempting to prepare double chlorides of manganese and lithium, and also of manganese and magnesium, a substance was obtained which proved to be manganous chloride with 2 mols. H_2O instead of

4 mols., which is the normal number. The substance forms slender, monoclinic prisms, and resembles ordinary manganous chloride, except that it does not lose water of crystallisation when dried over calcium chloride.

Manganous chloride combines with the chlorides of potassium, rubidium, and cæsium; but, following the groups of metals according to the periodic system, appears incapable of combining with any of the chlorides between cæsium and magnesium. The latter, however, marks the commencement of a new series, with every member of which manganous chloride can probably combine. The explanation of these facts is simple, if we assume that the acidic and basic powers of manganous chloride are about equal to those of strontium chloride, and that, in its compounds with the chlorides of potassium, rubidium, and cæsium, manganous chloride acts in its acidic capacity, whilst in its compounds with the chlorides of magnesium (zinc?), cadmium, &c., it acts in its basic capacity. Taking this view, it is easy to understand the break occurring between the two series.

The following table gives the double chlorides of manganese and potassium, ammonium, rubidium, and magnesium investigated by the author, and shows that there is a well marked regularity in the series.

$KMnCl_3 + 2H_2O$ (triclinic).	—	—
—	—	$(NH_4)_2MnCl_4 + 2H_2O$ (monoclinic).
—	—	$Rb_2MnCl_4 + 2H_2O$ (triclinic).
$CsMnCl_3 + 2H_2O$ (orthorhombic).	—	$Cs_2MnCl_4 + 2H_2O$ (triclinic).

$Mn_2MgCl_6 + 12H_2O$.
$Mn_2MgBr_6 + 12H_2O$.

Special efforts were made by the author to obtain both the missing compounds from the left-hand series, but without success. The entire dissimilarity in crystalline system and habit between the potassium and cæsium salt is remarkable, and indicates that, although chemically analogous, the compounds are not really very closely related to each other. G. T. M.

Nickel Potassium and Cobalt Potassium Fluorides. By C. Poulenc (*Compt. rend.*, **114**, 746—749).—When nickel chloride is heated with potassium hydrogen fluoride, decomposition takes place with evolution of hydrogen fluoride and considerable intumescence. The mixture is heated for about an hour at 220°, and afterwards is kept in fusion for about 10 minutes, and then cooled very slowly. The product is treated with water in order to remove potassium chloride, and *nickel potassium fluoride*, NiF_2,KF, is obtained in beautiful, green plates of sp. gr. 3·27. The compound is easily soluble in water, very slightly soluble in methyl or ethyl alcohol, insoluble in benzene and terebenthene. It dissolves in cold hydrofluoric acid and also in nitric and hydrochloric acids, the solubility in the latter cases increasing with the temperature. In contact with ammonia, the double fluoride gradually becomes violet-blue; when heated in presence of air,

potassium fluoride volatilises, and crystallised green nickel oxide is left; hydrogen reduces the salt at a red heat; fused alkaline carbonates produce nickel oxide and an alkaline fluoride; fused potassium hydrogen sulphate produces nickel sulphate and potassium fluoride.

Cobalt chloride, under similar conditions, yields *cobalt potassium fluoride*, CoF_2,KF, in garnet-red, crystalline plates of sp. gr. 3·22. In general properties it is strictly analogous to the nickel compound, but in its preparation alcohol must be used instead of water for the extraction of the potassium chloride in consequence of the difficulty of removing the water from the crystals of the double fluoride.

C. H. B.

Rhodosochromium Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **45**, 260—274; compare Abstr., 1885, 23).—*Rhodosochromium chloride* (roseochromium chloride) $(HO)_3(Cr_2,6NH_3)Cl_3 + 2H_2O$, is formed when a solution of chromammonium chloride in ammonium chloride oxidises spontaneously in sealed flasks; in the author's case, the change was allowed to progress for four years; at the end of this time, the mixture of rhodosochloride and ammonium chloride crystals which had separated were washed by decantation with successive small quantities of cold water acidified with hydrochloric acid, until all the ammonium chloride was dissolved; the rhodosochloride was then dissolved in water, reprecipitated by a saturated solution of ammonium chloride, and washed first with hydrochloric acid diluted with three times its volume of water, and finally with alcohol. The new salt crystallises in crimson, microscopic prisms; it gradually loses 1 mol. H_2O over oil of vitriol, and is slowly decomposed at 100°. One part of the salt dissolves in 10·6 parts of water at 18°; the solution decomposes when heated, becoming first grey, then green, and finally depositing all the chromium as hydroxide. Even at the ordinary temperature, the aqueous solution becomes alkaline and much bluer after 24 hours, and in a longer time deposits chromium hydroxide. The following reactions are obtained with a 4 per cent. cold aqueous solution, freshly prepared; unless otherwise stated, the precipitates are crimson and crystalline. Dilute nitric acid precipitates the nitrate even in very dilute solutions; concentrated hydrochloric acid yields no precipitate; concentrated hydrobromic acid throws down the bromide; solid potassium iodide causes the iodide to separate; dilute sulphuric acid, in the presence of alcohol, precipitates the hydrogen sulphate; ammonium sulphate precipitates the normal sulphate when the solution is stirred; sodium dithionate gives a precipitate which is doubtfully crystalline; hydrofluosilicic acid gives a doubtfully crystalline, bulky precipitate; hydrogen platinochloride gives a buff precipitate; mercuric chloride gives a lilac precipitate; hydrogen aurochloride gives almost immediately a brilliant, red-brown precipitate; potassium chromate precipitates a brilliant, red-brown chromate; potassium dichromate gives a voluminous, orange-yellow precipitate; sodium pyrophosphate gives a precipitate which dissolves in excess; disodium hydrogen phosphate gives no precipitate save in the presence of ammonia; ammonium thiocyanate gives a precipitate in concentrated solution; potassium ferrocyanide gives a lilac-red, and the ferricyanide a chamois-brown precipitate.

Of the salts precipitated as above the *aurochloride*,

$$(HO)_3(Cr_26NH_3)Cl_3,2AuCl_3 + 2H_2O,$$

the *platinochlorides*, $2[(HO)_3(Cr_26NH_3)Cl_3],3PtCl_4 + 6H_2O$ and $(HO)_3(Cr_26NH_3)Cl_3,PtCl_4 + 2H_2O$, the *bromide*, $(HO_3)(Cr_26NH_3)Br_3 + 2H_2O$, the *iodide*, $(HO)_3(Cr_26NH_3)I_3 + 2H_2O$, the *nitrate*, $(HO)_3(Cr_26NH_3)(NO_3)_3 + H_2O$, the *hydrogen sulphate*,

$$2[(HO)_3(Cr_26NH_3)H(SO_4)_2] + 3H_2O,$$

the *normal sulphate*, $2[(HO)_3(Cr_26NH_3)],3SO_4 + 5H_2O$, and the *chromate*, $2[(HO)_3(Cr_26NH_3)],3CrO_4 + 7H_2O$, were analysed and are fully described.

The *persulphide*, $2[(HO)_3(Cr_26NH_3)],S_{11} + 4H_2O$, is precipitated in red-brown, octahedral crystals on adding ordinary ammonium sulphide to a solution of the rhodosochloride and subsequently ammonium sulphide containing much sulphur. The *hydrogen oxalate*, $2[(HO)_3(Cr_26NH_3)],H_4(C_2O_4)_5 + 2H_2O$, is precipitated by adding the rhodosochloride to a cold solution of ammonium oxalate, filtering, and adding oxalic acid and alcohol. It forms crimson-red, rhombohedral prisms and rhombic tables. A. G. B.

Constitution of Cobalt, Chromium, and Rhodium Bases. By S. M. Jörgensen (*J. pr. Chem.* [2], **45**, 274—280; compare Abstr., 1883, 554, *J. pr. Chem.* [2], **42**, 206, and preceding abstract).—Inasmuch as rhodosochromium chloride yields chlorotetramine chromium chloride, $Cl{\cdot}Cr\left\{\begin{matrix}OH_2{\cdot}Cl\\NH_2{\cdot}NH_3{\cdot}NH_3{\cdot}NH_3{\cdot}Cl\end{matrix}\right.$, chromium chloride, ammonium chloride, and water when decomposed by hydrochloric acid, the two chromium atoms cannot be regarded as directly united in the rhodosochloride. The author regards this salt as constituted of the two monovalent residues $-Cr\left\{\begin{matrix}HO\\NH_3{\cdot}NH_3{\cdot}Cl\end{matrix}\right.$ and

$$-Cr\left\{\begin{matrix}OH_2{\cdot}Cl\\NH_3{\cdot}NH_3{\cdot}NH_3{\cdot}NH_3{\cdot}Cl,\end{matrix}\right.$$

united together by an atom of oxygen. So also he regards it as impossible that the chromium atoms in the erythro-salts (Abstr., 1883, 554) should be directly united, and points out that the erythrochloride probably consists of the two residues $-Cr\left\{\begin{matrix}OH_2{\cdot}Cl\\NH_3{\cdot}[NH_3]_3{\cdot}Cl\end{matrix}\right.$ and $-Cr\left\{\begin{matrix}NH_3{\cdot}Cl\\NH_3{\cdot}[NH_3]_3{\cdot}Cl,\end{matrix}\right.$ united by a NH group, in which the N, being unsaturated, readily combines with HCl. General formulæ are deducible from these considerations. A. G. B.

Chromosulphuric Acid and Metallic Chromosulphates. By A. Recoura (*Compt. rend.*, **114**, 477—479).—The green chromic sulphate, $Cr_2(SO_4)_3$, previously described (this vol., p. 411), combines in aqueous solution with sulphuric acid and various metallic sulphates to form compounds, such as $Cr_2(SO_4)_3,K_2SO_4$, from which the

sulphuric acid is not at once precipitated by barium salts, although the metal introduced with the sulphate may be recognised by means of the usual tests. Hence these compounds may be regarded as salts of a complex acid, chromosulphuric acid, $H_2Cr_2(SO_4)_4$, resembling hydrochromocyanic and chromoxalic acids. The chromosulphates are not, however, very stable substances, as the sulphuric acid is gradually precipitated by barium chloride even in the cold, and at once on heating.

Chromosulphuric acid, $H_2Cr_2(SO_4)_4,11H_2O$, is prepared by reducing chromic acid (50 grams) in the cold with alcohol (15 c.c. of 95 per cent.) and sulphuric acid (50 c.c.) in the presence of a minimum quantity of water (25 c.c.). The green, syrupy liquid thus obtained is evaporated to dryness, and the residue extracted with glacial acetic acid, which yields a solution from which the acid is obtained as a green, hygroscopic powder on evaporating the solvent in a vacuum. Chromosulphuric acid is stable in dry air, but unstable in aqueous solution, in which it gradually changes into the violet chromic sulphate previously described (*loc. cit.*).

Potassium chromosulphate, $K_2Cr_2(SO_4)_4,4H_2O$, is best prepared by heating chrome alum, first to 90°, when it loses half its water of crystallisation (12 mols.), and then to 110°, when it loses a further quantity (8 mols.). It dissolves slowly in cold water to a solution which does not yield a precipitate with barium chloride, but is at once precipitated by platinic chloride or picric acid. The *ammonium* and *sodium* salts are similar green powders.

Another way of preparing these alkali salts consists in reducing the dichromates with alcohol and sulphuric acid as in preparing the chrome alums, but in the presence of a small quantity only of water.

Other compounds similar to chromosulphuric acid, but containing more sulphuric acid, have been prepared. Jn. W.

Note by Abstractor.—Chromosulphates were described by Cross and Higgins in 1882 (Trans., 1882, 113).

New Series of Fluoroxy-compounds of Molybdenum. By A. Piccini (*Real. Accad. Linc.*, 7, i, 267—268).—When potassium fluoroxymolybdate, $MoO_2F_2,2KF + H_2O$, is dissolved in warm hydrogen peroxide solution (4 per cent.) oxidation occurs, and a salt of the composition $MoO_3F_2,2KF + H_2O$ separates out on cooling in splendid yellow laminæ. It is not altered by contact with air, and is very soluble in hot water, sparingly so in cold water. On heating at 100°, it loses water, and at 120° it gives off oxygen, leaving a white residue of $MoO_2F_2,2KF$, which falls to powder on cooling, and on prolonged heating yields potassium molybdate. The new salt reduces potassium permanganate in dilute sulphuric acid solution with evolution of oxygen.

The author proposes to prepare and study salts of analogous composition to the one now described. W. J. P.

Double Halogen Salts of Tin. By G. M. Richardson (*Amer. Chem. J.*, **14**, 89—107; compare Remsen, this vol., p. 779).—The double halogen salts described in this paper were prepared, in most

cases, by mixing the solutions of the constituent halogen salts. The alkali halogen salt was dissolved in water, and the tin solution was prepared by dissolving the metal in hydrochloric acid or hydrobromic acid until the liquid no longer contained free acid.

Potassium stannochloride, $KSnCl_3,H_2O$, is obtained on mixing potassium chloride with a large excess of stannous chloride. It forms white, hair-like crystals, which do not lose water when allowed to remain over sulphuric acid, and dissolves in hot potassium chloride solution, and in hot hydrochloric acid, with formation of *dipotassium stannochloride*, $K_2SnCl_4,2H_2O$, which crystallises out on cooling in large, white, orthorhombic plates [$a : b : c = 0{\cdot}685231 : 1 : 0{\cdot}758634$]. It also crystallises with 1 mol. H_2O.

Stannous chloride unites with ammonium chloride, and stannous bromide with potassium bromide and with ammonium bromide, to form double halogen salts, which are analogous to the potassium salts above described. In the case of the chlorides, the tendency to form the salt with 2 mols. of the alkali chloride is very strong, and is even more marked in the case of ammonium chloride than in that of potassium chloride. With the bromides, on the other hand, the tendency is to form the salt with 1 mol. of the alkali bromide, whilst the one containing 2 mols. of the alkali bromide is obtained with greater difficulty, and in this case also the salt with 2 mols. of ammonium bromide is much more readily obtained than the potassium salt.

No salts of definite composition could be obtained by mixing solutions of stannous bromide and potassium chloride, or of stannous chloride and potassium bromide; and the double halogen salts of tin with lithium and sodium, if formed at all, were so soluble that they refused to crystallise. G. T. M.

Fluoroxyvanadates, Fluoroxyhypovanadates, and Fluorovanadites. By A. Piccini and G. Giorgis (*Gazzetta*, **22**, i, 55—96; compare Abstr., 1889, 214).—The authors have re-examined a number of vanadium fluorine compounds on account of the discrepancies between the results previously obtained by them (Abstr., 1889, 214) and those obtained by Ditte, Petersen, and Baker (Abstr., 1888, 114, 558; 1889, 107; 1890, 15; and Trans., 1879, 760). In analysing these compounds, the fluorine was determined by Penfield's method, the vanadium by Gerland and Gibbs' process, and the alkalis by Roscoe's method (this Journal, 1871, 28); the vanadic anhydride used in the preparations was obtained by carefully calcining pure ammonium metavanadate repeatedly precipitated from its aqueous solution by ammonium chloride; the compounds corresponding with the lower oxides of vanadium were obtained by reducing solutions of pure vanadates by the electric current. For this purpose a battery of about 20 Daniell cells is sufficient.

The solution of pure vanadic anhydride in hydrofluoric acid is not greenish, as stated by Ditte and Petersen, but yellow, the colour being very faint when very strong hydrofluoric acid is used, and becoming more intense on diluting the solution.

Octahedral ammonium fluoroxyvanadate, $VO_2F,3NH_4F$, is prepared by dissolving vanadic acid in excess of hydrofluoric acid and exactly

neutralising the hot solution with ammonia. Baker assigns the formula $12NH_4F,V_2O_5,2VOF_3$ to this substance. It crystallises in octahedra and not in a rhombic form, as stated by Petersen; after pressing between filter-paper, the crystals only lose 0·34 per cent. of their weight at 100°, and finally they may be calcined with care without any loss of vanadium.

Lamellar ammonium fluoroxyvanadate, $2VO_2F,3NH_4F$, may be obtained by heating an aqueous solution of the preceding compound on the water-bath. It is prepared by dissolving vanadic anhydride in a slight excess of hydrofluoric acid, adding ammonium fluoride in the proportion of $1\frac{1}{2}$ mols. per mol. of vanadium, and concentrating the solution. It crystallises in thin, yellowish, nacreous laminæ, and may be recrystallised unaltered from an aqueous solution; it only loses slightly in weight at 100°, but gives off white fumes containing vanadium if rapidly heated to 300°; when gently heated, it may be calcined without loss. Petersen assigns to this compound the formula $HF,7NH_4F,4VO_2F$.

Acicular ammonium fluoroxyvanadate, $2VOF_3,3NH_4F,H_2O$, is obtained by dissolving the octahedral salt in 10 per cent. hydrofluoric acid, and gently evaporating on the water-bath; on cooling, a deposit is formed of pale yellowish, acicular prisms, which have a silky appearance when dry, attack glass, possess an odour of hydrofluoric acid, and are decomposed by sulphuric acid. It is decomposed by crystallisation from water or hydrofluoric acid. It is also decomposed at 100°, but may be calcined with care without loss of vanadium. This compound may possibly be that obtained by Petersen by adding not too large an excess of ammonium fluoride to a hydrofluoric solution of vanadic anhydride and concentrating, a product which was said to have the formula $3HF,9NH_4F,5VOF_3$, but which the author has not succeeded in preparing.

Lamellar potassium fluoroxyvanadate, $2VO_2F,3KF$, obtained by dissolving vanadic anhydride in a hot solution of potassium fluoride, crystallises in yellowish, nacreous plates, dissolves in water, forming an intense yellow solution, attacks glass very slightly, and is only slightly affected by sulphuric acid; it does not lose weight at 100°, or on ignition. Baker assigns the formula $6KF,V_2O_5,2VOF_3 + 2H_2O$ to this compound. The authors have found it impossible to prepare in a state of even approximate purity the compounds $2KF,VOF_3$ and $4KF,VF_5,VF_3$ obtained by Petersen by adding a solution of potassium fluoride to a hydrofluoric solution of vanadic anhydride.

On dissolving the compound $2VO_2F,3KF$ in a hot solution of hydrofluoric acid, and allowing the solution to cool, an acicular salt crystallises out, having approximately the composition

$$HF,3KF,2VOF_3.$$

After standing for a long time, this substance appears to have the composition $2VOF_3,3KF + H_2O$.

Sodium fluoroxyvanadate, $VOF_3,VO_2F.3NaF,H_2O(?)$, is prepared by dissolving sodium carbonate (3 mols.) and vanadic anhydride (2 mols.) in distilled hydrofluoric acid, evaporating on the water-bath until every 100 c.c. of solution contains about 10 grams of

vanadic anhydride, and allowing the solution to remain for a few days. The liquid is then decanted from the crystalline deposit formed and allowed to evaporate spontaneously. After a time yellowish-white, bulky, tabular prisms of the sodium salt are formed, which, however, are very unstable, and turn green and give off an odour of hydrofluoric acid even during drying.

Zinc fluoroxyvanadate, $VO_2F,ZnF_2,7H_2O$, prepared by Baker's method, has the preceding formula. It is very soluble in water, and crystallises in hard, rhombic prisms which rapidly alter on exposure to the atmosphere, becoming coated with a reddish film.

Octahedral ammonium fluoroxyhypovanadate, $VOF_2,3NH_4F$, may be obtained by the electrolytic reduction of a solution of ammonium metavanadate acidified with hydrofluoric acid, and containing ammonium fluoride. The liquid turns blue after a time, and a blue, crystalline deposit is produced. It may also be prepared by reducing vanadic acid with alcohol and adding ammonium fluoride, or by dissolving ammonium metavanadate in dilute hydrofluoric acid, reducing with sulphurous anhydride, neutralising with ammonia, and adding ammonium fluoride. It forms blue, octahedral crystals, soluble in water, but insoluble in a solution of ammonium fluoride. It remains unaltered at 100°, but decomposes on heating strongly. The monoclinic salt, $VOF_2,2NH_4F,H_2O$, may be obtained by dissolving the preceding salt in hot hydrofluoric acid.

Potassium fluoroxyhypovanadate, $VOF_2,2KF$, is obtained in sky-blue crusts by treating a solution of ammonium metavanadate reduced by sulphurous anhydride with potassium fluoride. Petersen's compound, $8NaF,3VOF_2,2H_2O$, could not be isolated in a state of sufficient purity.

Zinc fluoroxyhypovanadate, $VOF_2,ZnF_2,7H_2O$, is prepared by the electrolytic reduction of a hydrofluoric solution of vanadic acid and zinc oxide in molecular proportions. The liquid becomes successively blue and green; a deposit of blue, prismatic crystals is then formed, if the solution is sufficiently concentrated. It is soluble in cold water, but partially decomposes on boiling, except in the presence of hydrofluoric acid. The aqueous solutions are slowly oxidised on standing. When acidified with sulphuric acid, they reduce solutions of potassium permanganate. The salt loses 6 mols. H_2O at 100°, and becomes decolorised, but it regains its colour on re-hydration. On treating it with nitric acid, it is oxidised, and on evaporating to dryness, the residue has the composition $V_2O_5,2ZnO$.

The *cadmium* salt, $VOF_2,CdF_2,7H_2O$, is prepared in a similar manner to the zinc salt, and has similar properties.

Cobalt fluoroxyhypovanadate, $VOF_2,CoF_2,7H_2O$, is obtained by dissolving vanadic anhydride in hydrofluoric acid, adding a little less than a molecular proportion of cobalt carbonate and reducing electrolytically. When the solution becomes of an intense blue colour, it is filtered and concentrated. The salt crystallises in bottle-green prisms which have a violet reflex, and yield a rose-coloured powder. It commences to lose weight at 80°, and becomes anhydrous at 160°.

Nickel fluoroxyhypovanadate, $VOF_2,NiF_2,7H_2O$, is obtained like the preceding compound, and forms green crystals isomorphous with those of the cobalt salt.

Zinc fluorovanadite, $VF_3,ZnF_2,7H_2O$, is obtained by prolonging the action of the electric current in the preparation of zinc fluoroxyhypovanadate until the blue liquid turns green. On concentrating the solution, the zinc salt is deposited in minute, lustrous crystals which lose the greater part of their water of hydration at 100°. It is partially oxidised by the air, and energetically by nitric acid.

The *cadmium* salt, $VF_3,CdF_2,7H_2O$, generally resembles the zinc salt; it is green, sparingly soluble in water, and its solution is oxidised on exposure to the air.

In conclusion, the authors point out that in the elements vanadium, niobium, and tantalum the tendency to form highly fluorinated compounds increases with the atomic weight of the element; thus, whilst VO_2F is not affected by small quantities of hydrofluoric acid, NbO_2F is converted into $NbOF_3$, and $TaOF_3$ into TaF_5. The formation of the three zinc compounds, $VO_2F,ZnF_2,7H_2O$, $VOF_2,ZnF_2,7H_2O$, and $VF_3,ZnF_2,7H_2O$, which all crystallise with the same amount of water, contain the same number of atoms, have similar crystalline habits, and are geometrically isomorphous, seems to indicate that an atom of fluorine may in many cases be substituted for an atom of oxygen without altering the essential character of the compound.

S. B. A. A.

Double Halogen Salts of Antimony. By C. E. Saunders (*Amer. Chem. J.*, **14**, 152—164; compare Remsen, this vol., p. 779).—The double chloride of antimony and cæsium to which Godeffroy (*Zeit. allg. österr. Apotheker-Vereins*, 1874, 161) gave the formula $SbCl_3,6CsCl$, has really the formula $Cs_3Sb_2Cl_9$. It crystallises in elongated, orthorhombic prisms, which are sometimes twinned, giving a rough, pseudo-hexagonal appearance, and is the only compound of cæsium chloride and antimony chloride that can be easily obtained. Similarly, the double chloride of antimony and rubidium, described by that author (*ibid.*, 1875, 21), has, most probably, the formula $Rb_{23}Sb_{10}Cl_{53}$. It crystallises in pseudo-hexagonal, superposed plates, and is so stable that it may be heated to a temperature of nearly 230° without undergoing change. Rubidium chloride and antimony chloride also combine to form the double salts $Rb_5Sb_3Cl_{14}$ and $RbSbCl_4$. The former was obtained as pale-yellow crystals, resembling rhombohedra in general shape; the latter in apparently orthorhombic, colourless crystals, which, when freshly made, had brilliant faces, but soon became opaque on exposure to air.

G. T. M.

Double Halogen Salts of Bismuth. By C. P. Brigham (*Amer. Chem. J.*, **14**, 164—182; compare Remsen, this vol., p. 779).—Of the three previously described double chlorides of bismuth and potassium, only one, namely, that prepared by Jacquelaine (*Ann. Chim. Phys.*, **66**, 113), of the formula $BiK_2Cl_5 + 2H_2O$, really exists. A salt of the composition $BiKCl_4 + H_2O$, which loses half a molecule of water of crystallisation, when dried over calcium chloride, is obtained when bismuth oxide (5 mols.) and potassium chloride (4 mols.) are dissolved in hot hydrochloric acid, and the solution is evaporated until, on cooling, a mass of fibrous needles, radiating from centres, crystallises out.

The salts to which Godeffroy has attributed the formulæ Rb_6BiCl_9 and Cs_6BiCl_9 do not really exist, the latter formula having been given to a mixture of the two compounds Cs_3BiCl_6 and $Cs_3Bi_2Cl_9$. Of these, the former crystallises in thin, transparent plates, and the latter in elongated, yellow prisms.

Bismuth chloride forms, with rubidium chloride, the salts Rb_3BiCl_6, $Rb_{23}Bi_{10}Cl_{53}$, and $RbBiCl_4 + H_2O$, of which the two latter correspond with the double chlorides of antimony and rubidium described by Saunders (preceding abstract).

As the atomic weight of the alkali in combination with bismuth increases, the amount of water of crystallisation decreases, thus:— $BiCl_3,2NaCl + 3H_2O$; $BiCl_3,2KCl + 2H_2O$; $BiCl_3,RbCl + H_2O$; $BiCl_3,3CsCl$. G. T. M.

Preparation and Assaying of Pure Platinum. By F. Mylius and F. Foerster (*Ber.*, **25**, 665—686).—This paper contains first an account of the method for assaying platinum, elaborated by Stas and Deville, in connection with the preparation of the standards for the International Committee of Weights and Measures. An idea of the accuracy of their method is given by the following figures, which represent the results of an analysis of a metre-rod:—

	Deville.	Stas.
Platinum	89·8200	89·8520
Rhodium	0 1300	0·1350
Ruthenium	0·0290	0·0386
Iron	0·0748	0·0506
Iridium	9·8560	9·8652
	99·9098	99·9414

The authors have examined the delicacy of this method by preparing the pure metals, mixing a known small quantity of each with a known weight of platinum, and then estimating this quantity by the Stas-Deville method. To obtain the mixture, a known weight of platinum sponge was impregnated with a solution containing a known weight of the other metal, and the whole was dried, and ignited in a current of hydrogen. The determination of ruthenium and iridium is accurate, and so is that of rhodium, with practice; palladium cannot be so accurately determined. The determination of iron is also accurate; that of copper is less so.

A new method is then proposed for the examination of platinum containing only small quantities of impurities. It is placed in a porcelain boat inside a glass tube, which is heated to about 238° by quinoline vapour, and first chlorine and then a mixture of chlorine with carbonic oxide (and anhydride) is passed over it; the platinum volatilises, and the residue in the boat is examined for impurities. Iridium, however, also volatilises to some extent with the platinum; so do palladium, ruthenium, osmium, gold, and iron; but rhodium, silver, copper, lead, and zinc do not volatilise at all. By combining this method with that of Stas and Deville, the presence of the following quantities of impurities may be detected:—

Iridium	0·003 per cent.
Ruthenium	0·005 ,,
Rhodium	0·004 ,,
Palladium	0·01 ,,
Iron	0·001 ,,
Copper	0·002 ,,
Silver	0·002 ,,
Lead	0·002 ,,

The following, hitherto unpublished, method of Finkener's for obtaining platinum free from impurities, especially iridium, is then described; it depends on recrystallisation of sodium platinochloride. Commercial purified platinum is dissolved in *aqua regia*, to the solution of the chloride, freed from oxides of nitrogen, the calculated amount of pure sodium chloride is added, the solution is concentrated to a small bulk, and allowed to cool whilst being continuously stirred. The crystals which separate are freed from mother liquor by suction, washed with a concentrated solution of sodium chloride, and dissolved in a 1 per cent. solution of sodium carbonate. The solution is allowed to cool, when the salt again separates out. It is then dried at 120°, reduced in a current of hydrogen at a low temperature, and the platinum sponge thus obtained is washed for a long time with water, and finally dried and ignited. The metal thus obtained was extremely pure; no impurities could be detected in it by the methods mentioned above, and the authors consequently calculate that it contains at least 99·99 per cent. of platinum.

It may be of interest to mention that pure platinum is now prepared in Germany. The method of purification is simpler than the English one, not involving the use of lead, and it yields a very pure product. In a sample of 40 grams, no palladium or rhodium could be detected, and only a trace of iridium. A trace of iron, at most 0·001 per cent., was, however, present.

For further details of the different processes, the original paper must be consulted. C. F. B.

Mineralogical Chemistry.

Breithauptite from Sarrabus, Sardinia. By E. Mattirolo (*Real. Accad. Linc.*, **7**, iii, 98—100).—The mineral is found, together with small quantities of ulmannite, stephanite, discrasite, argentite, and native silver, imbedded in a matrix of calcite. It has the hardness 4·5, the sp. gr. 8·42, and occurs in ill-defined, fragile crystals. From the following analysis, it will be seen to have approximately the theoretical composition NiSb, assigned to breithauptite:—

	Sb.	As.	Ni.	Co.	S, Ag, and Pb.
Per cent.	65·07	0·20	32·94	0·29	traces

W. J. P.

Microscopic Structure of the Oölitic Iron Ore of Lorraine. By Bleicher (*Compt. rend.*, **114**, 590—592).—Microscopic examination, aided by previous calcination and treatment with acids and alkalis, shows that the ferruginous oölites of Lorraine, Mazenay, Pulnoy, and other oölites of the same horizon, are all constructed on the same type. They consist of a simple or compound inorganic or organic nucleus surrounded by regular concentric layers of a substance rich in silica and organic matter, in which microscopic, hyaline grains of sand and regular, rod-like forms can be recognised. The iron oxide seems to be enclosed between these concentric layers.

C. H. B.

Distribution of Titanic Oxide upon the Surface of the Earth. By F. P. Dunnington (*Amer. J. Sci.*, **42**, 491—495).—In view of the rare mention of titanic oxide as a constituent of rocks, the author has analysed 80 specimens of soil and rocks from points scattered over the earth's surface. Specimens 1 to 17 are from Virginia, the average percentage of titanic oxide found being 1·57. Nos. 18 to 40 are from other portions of the United States; average 0·85 per cent. Nos. 41 to 45 are from Oceania and Asia; average 0·90 per cent. Nos. 46 to 72 are soils from Europe; average 0·54 per cent. These results apply to air-dried soil. The wide distribution of titanic oxide in soils naturally suggested the examination of the rocks themselves. The author has therefore analysed eight typical rocks, the localities of which have previously furnished samples for published analyses. The average percentage of titanium oxide found was 0·56, notwithstanding the fact that in only two cases is titanium oxide noted in the published analyses.

B. H. B.

Heintzite, the New Borate from Leopoldshall. By W. Feit (*Chem. Zeit.*, **15**, 115).—Luedecke has found, inside a lump of pinnoïte collected near Leopoldshall, crystals of a mineral which he has called heintzite. This mineral has the appearance of clear, transparent gypsum, and is remarkably cleavable. The author has, however, little doubt that it is identical with the one discovered by him in 1889, and which he called kaliborite.

The author's view is supported not only by chemical analysis, but also by Luedecke's crystallographic measurements. The specific gravity and the hardness of the two minerals also agree.

L. de K.

Heintzite, the New Borate from Leopoldshall. By O. Luedecke (*Chem. Zeit.*, **15**, 222).—The author, in reply to Feit (see preceding abstract), admits that the chemical composition of kaliborite and heintzite is practically identical, both containing about the same percentage of boric acid, potash, magnesia, and water. This does not, however, prove them to be the same mineral. Whilst kaliborite occurs in badly-formed, crystalline crusts on the surface of pinnoïte, heintzite, which is found in the inside, forms well-made crystals with shining faces, and is readily cleavable in three directions. The author does not attach much importance to the similarity in specific gravity of the two minerals.

L. de K.

Ascharite, a New Borate. By W. Feit (*Chem. Zeit.*, **15**, 327).—Boracite and stassfurtite found in the neighbourhood of Aschersleben (Ascharia) occasionally contain a good many white lumps of a remarkably low specific gravity. They are externally covered with kainite and rock-salt, and so incorporated with potassium, sodium, and magnesium chlorides that these can scarcely be recognised with the naked eye. The insoluble residue is, however, quite unlike a similar compound obtained by treating stassfurtite with water. The latter looks like a fine mud and contains about 8 per cent of chlorine, whilst the former is composed of small fragments, easily reducible to an impalpable powder by pressure with the hands, and free from chlorine. A complete analysis proved that the author has come across a new mineral which, although only consisting of crystallised magnesium borate, has a composition different from that of similar known minerals, as its formula was found to be $3Mg_2B_2O_5 + 2H_2O$. The mineral is pure white and practically insoluble in water, to which, however, it communicates an alkaline reaction. Dilute mineral acids gradually dissolve it on warming. Its specific gravity varies between 1·85 and 1·95, according to its freedom from adhering salts. Before the blowpipe, it fuses to a white looking mass, without communicating a green colour to the flame. L. de K.

Barytes from Missouri. By C. Luedeking and H. A. Wheeler (*Amer. J. Sci.*, **42**, 495—498).—A variety of barytes is found in Pettis Co., Missouri, which presents peculiar chemical and crystallographical characteristics. The peculiarity is the occurrence of white to yellowish thin bands in an otherwise normal colourless barytes, and analysis shows that these bands consist of a mixture of barium and strontium sulphates with slight amounts of calcium and ammonium sulphates, the general character of the white barytes being shown by the following analytical results:—

$BaSO_4$.	$SrSO_4$.	$CaSO_4$.	NH_4SO_4.	H_2O.	Total.
87·2	10·9	0·2	0·2	2·4	100·9

The occurrence of ammonium sulphate in barytes has not hitherto been observed. The isomorphism of ammonium sulphate, mascagnite, with barytes, is worthy of notice. B. H. B.

Synthesis of Crocoïte and Phœnicocroïte. By C. Luedeking (*Compt. rend.*, **114**, 544—545).—When a solution of lead chromate in potassium hydroxide is exposed to the air for some months in a vessel with a flat bottom, a mixture of crystals of crocoïte and phœnicocroïte is obtained. With an excess of lead chromate mixed with potassium chromate, crocoïte alone is formed in highly modified, oblique, rhombic prisms, with an adamantine lustre and a hyacinth-red colour; it is stable when exposed to air. With a large excess of concentrated potash solution, phœnicocroïte is the sole product; it forms cochineal-red tables which have a resinous lustre and seems to belong to the rhombic system. When exposed to the air, the crystals alter and form a yellow powder.

If a solution of a caustic alkali saturated with litharge is exposed to the air for several months, crystals of lead hydroxide, $2PbO,H_2O$, are obtained, but no cerussite is formed. C. H. B.

Hübnerite, Hessite, Bismutite, and Natrolite. By F. A. Genth (*Amer. J. Sci.*, **43**, 184—189).—1. *Hübnerite.*—The author gives crystallographical descriptions and analyses of hübnerite from (*a*) the North Star Mine, Silverton, Colorado; (*b*) Cement Creek, near Silverton; (*c*) Bonito Mountain, New Mexico; and (*d*) Monmouth District, Nevada. The analytical results were as follows:—

	WO_3.	FeO.	MnO.	CaO.	MgO.	Total.
a.	74·75	2·91	21·93	0·11	trace	99·70
b.	76·63	1·61	21·78	0·09	trace	100·11
c.	76·33	3·82	19·72	0·13	trace	100·00
d.	74·88	0·56	23·87	0·14	0·08	99·53

2. *Hessite from Mexico.*—A specimen of hessite from the Refugio Mine, Jalisco, contains 62·80 per cent. of Ag_2Te, 1·96 per cent. of PbTe, with 1·40 per cent. of tellurium, probably present as tellurous oxide.

3. *Bismutite.*—Associated with the phenacite of Mount Antero, Colorado, is a greyish or yellowish-green mineral of prismatic form. Of this the author gives the results of two analyses; but the material is too impure to admit of the deduction of a formula.

4. *Natrolite.*—This mineral occurs at Magnet Cove, Arkansas, in association with ægirite, eudialyte, and titanite, in large, colourless, cleavable masses. The sp. gr. is 2·243, and analysis gave:—

H_2O.	SiO_2.	Al_2O_3.	Na_2O.	Total.
9·81	47·97	26·51	15·98	100·27

B. H. B.

Chemical Composition of Iolite. By O. C. Farrington (*Amer. J. Sci.*, **43**, 13—16).—As is well known, the formula of iolite has never been satisfactorily established, chiefly for the reason that the state of oxidation of the iron, in the analyses hitherto published, has not been determined. The exceptional purity of the iolite described by E. O. Hovey (Abstr., 1889, 25) as a rock-forming mineral at Guilford, Connecticut, induced the author to make an analysis of it. The results obtained he tested by comparison with an analysis of iolite from Haddam, Connecticut, and he concludes that the formula of iolite is $H_2O,4(MgFe)O,4Al_2O_3,10SiO_2$. B. H. B.

Chloritoïd, Grünerite, and Riebeckite from Michigan. By A. C. Lane, H. F. Keller, and F. F. Sharpless (*Amer. J. Sci.*, **42**, 499—508).—1. *Chloritoïd* has been known to occur in the upper peninsula of Michigan for some years. Recently it has been found in large, dark-green plates at the Champion iron mine. On analysis, it gave results from which the formula $H_{16}Fe_7Al_{16}Si_8O_{55}$ is deduced, a formula nearly identical with that now generally accepted for sismondine.

2. *Grünerite.*—There is a peculiar amphibole, associated with certain Lake Superior iron ores, which has been described as actinolite and as anthophyllite. In reality, it is a ferro-magnesian monoclinic amphibole, corresponding closely with the description of grünerite given by Lacroix. Analysis shows very clearly, by the absence of calcium, that the mineral is not actinolite.

3. *Riebeckite* or *crocidolite.*—Mr. Lane notes a new occurrence of this group of amphiboles, namely, as a secondary fibrous growth on the primary hornblende of syenite. B. H. B.

Tschermak's Theory of the Chlorite Group and its Alternative. By F. W. Clarke (*Amer. J. Sci.*, **43**, 190—200).—In his latest paper, Tschermak endeavours to explain the chemical structure of the chlorites by dividing this group of minerals into two subgroups, orthochlorites and leptochlorites. The orthochlorites are represented as mixtures of two end products, serpentine and amesite; whilst for the leptochlorite, in addition to the serpentine and amesite molecules, four other fundamental compounds are assumed: strigovite, chloritoïd, and two derivatives of amesite. If this mode of interpretation is the only one possible, the problem of the chlorite group is solved. But if other schemes can be devised representing the facts equally well, further investigation becomes necessary. The known facts, the author believes, are fairly well sustained by his hypothesis that the more complex silicates are merely substitution derivatives of normal salts. The author adduces, at great length, the arguments in favour of his view, and between the two theories, experimental research must be the final arbiter. Until experiment has given grounds for decision, either theory may properly be used as a guide. B. H. B.

Iron Ores of the Marquette District, Michigan. By C. R. Van Hise (*Amer. J. Sci.*, **43**, 116—132).—From the results of a systematic investigation of the entire Marquette district, the author concludes that the original rock of the iron-bearing formation was a cherty iron carbonate, and that the varieties of rock now found in this formation, such as chert, jasper, schists, and ore, were all produced from this original carbonate by various alterations. The form, position, and relation of the ore deposits render it evident that the origin was not eruptive, and it is equally certain that these irregular masses of ore were not produced directly by sedimentation. All the facts bear towards the conclusion that the ore is a secondary concentration produced by the action of water percolating downwards. The same view applies to the other iron-bearing districts of Lake Superior. B. H. B.

New Meteoric Iron from Maryland. By A. E. Foote (*Amer. J. Sci.*, **43**, 64).—Three or four years ago a meteoric iron mass was ploughed up in Garrett Co., Maryland. It contains over 11 per cent. of nickel and cobalt, the proportion of the latter being unusually high. It is one of the best octahedral etching irons known, being even more characteristic than most of those that have been used for printing directly on paper. Besides the octahedral structure, it also shows a

large number of secondary lines regularly disposed with reference to the principal markings, similar to those described by J. Lawrence Smith in a Wisconsin meteorite in 1869, under the name of Laphamite markings. The original weight of the mass was 45 oz., and its present weight is $36\frac{1}{2}$ oz. The paper is illustrated by photographs of the etched surface and of the entire mass. B. H. B.

Aërolite from Kansas. By G. F. Kunz and E. Weinschenk (*Amer. J. Sci.*, **43**, 65—67).—On June 25, 1890, a meteorite was observed travelling from south to north, and the largest portion, weighing 180 lbs., fell at Farmington, Washington Co., on the farm of W. H. January, who witnessed the actual fall. The sound of the explosion was heard throughout a number of counties in Kansas and Nebraska. The approximate composition of the mass is as follows:—

Nickeliferous iron	7·7
Troïlite	5·0
Siliceous part insoluble in HCl....	46·0
Siliceous part soluble in HCl.....	41·5

The iron gave, on analysis, the following results:—

Fe.	Ni.	Co.	Total.
86·76	12·18	0·83	99·77

The siliceous part yielded the following results:—

	SiO_2.	FeO.	Cr_2O_3.	Al_2O_3.	MnO.	NiO.	CaO.	MgO.
I.	38·50	23·54	—	—	0·34	0·69	0·12	36·81
II.	53·80	11·98	1·41	4·32	trace	—	4·08	22·37

	K_2O.	Na_2O.	Total.
I.	—	—	100·00
II.	0·27	1·77	100·00

I Portion soluble (olivine), II portion insoluble, in hydrochloric acid.

As is generally the case in stony meteorites, the nickel-iron shows a higher percentage of nickel and cobalt than is usual in meteoric irons. The meteorite belongs to the black chondrites, and has the greatest resemblance to the meteorite of Sevenkof. B. H. B.

Meteorite of Jelica. By S. M. Losanitsch (*Ber.*, **25**, 876—880).—The Jelica meteorite consists of a soft, grey mass, including several pieces of a brown material which scarcely differs in composition from the grey mass, but contains a slightly larger proportion of metasilicates. The specific gravity of the grey mass = 3·439, that of the brown substance = 3·466 at 18·6° C.

Before analysis, the hard outside crust was removed.

It contains:—

Metals ..	2·49 p. c.	Silicates sol. in HCl	54·00 p. c.
Troïlite..	7·09 ,,	Silicates insol. in HCl...	36·25 ,,
Chromite.	0·15 ,,	Alkali and organic matter	0·12 ,,

The author considers that the last has been absorbed by the meteorite from the damp ground.

The metals, on analysis, gave 66·44 per cent. Fe, 33·47 per cent. Ni, 2·09 per cent. Co, and a trace of copper. It is noteworthy that the percentage of nickel and cobalt is high. The proportion of iron to nickel nearly corresponds with that required by the formula Fe_2Ni.

E. C. R.

"Julianen" and "Georgen" Springs in the Royal Bath at Eilsen. By R. Fresenius (*J. pr. Chem.* [2], **45**, 287—296).—The "Julianen" spring yields 40·6 cub. ft. of water per hour. The water is quite clear and colourless; it smells strongly of hydrogen sulphide; its temperature was 17° on June 20, 1890, the air temperature being 11·45°; its sp. gr. was 1·003087 at 17·5°. The "Georgen" spring yields 196·2 cub. ft. of water per hour; the water is clear and colourless, and smells strongly of hydrogen sulphide; the temperature of the water on 21st of June, 1890, was 20°, the temperature of the air being 12·1°; the specific gravity was 1·002980 at 17·5°. The following table shows the quantity of salts, &c., in grams, per 1000 grams of these waters; the salts are represented as anhydrous, and the carbonates as anhydrous bicarbonates:—

	Julianen.	Georgen.
Calcium sulphate	2·093951	1·948343
Strontium sulphate	0·019430	0·026041
Magnesium sulphate	0·178739	0·246104
Sodium sulphate	0·020005	0·123453
Potassium sulphate	0·009416	0·011669
Sodium chloride	0·190872	0·106852
Lithium chloride	0·000662	0·001290
Ammonium chloride	0·001438	0·002207
Sodium iodide	0·000005	0·000005
Sodium bromide	0·000584	0·000493
Magnesium bicarbonate	0·476858	0·416285
Ferrous bicarbonate	0·001316	0·000684
Manganous bicarbonate	0·000058	0·000061
Calcium borate	0·001024	0·002669
Calcium silicate	0·046301	0·052376
Aluminium phosphate	0·000155	0·000060
Alumina	0·000126	0·000136
Total	3·040940	2·938728
Free carbonic anhydride	0·104164	0·029237
Hydrogen sulphide	0·049747	0·046749
Light hydrocarbons	0·002145	0·000198
Nitrogen	0·027318	0·021298
Total	3·224314	3·036210

Traces of formic acid and other volatile organic acids, of resins, and of "extractive" were detected in both waters. A. G. B.

Organic Chemistry.

Boiling Points of Paraffin Derivatives. By G. Hinrichs (*Compt. rend.*, **114**, 597—599).—The formula previously applied (Abstr., 1891, 1330) to the calculation of the boiling points of the normal paraffins is now shown to hold good for monosubstitution derivatives in which halogen, hydroxyl, amidogen, phenyl, or cyanogen has been substituted for hydrogen in the terminal group of the paraffin chain. C. H. B.

Carbon Chlorobromides. By A. Besson (*Compt. rend.*, **114**, 222—224).—See p. 771.

Pyrogenic Hydrocarbons in Compressed Gas. By A. Brochet (*Compt. rend.*, **114**, 601—603).—The only definite hydrocarbons known to exist in compressed gas prepared by the distillation of Boghead cannel or of shale oils are normal hexylene and erythrene. The author finds that the other olefines present are normal butylene (b. p. 166°), normal amylene $\alpha\beta$ (b. p. 39—40°), and normal amylene $\beta\gamma$ (b. p. 35—36°). He also found piperilene, $CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$, boiling at 41—42°, and confirms the presence of erythrene and normal hexylene. It is especially noteworthy that all the olefines formed after the prolonged action of a high temperature are primary, without any lateral chains. C. H. B.

Action of Metals on Salts Dissolved in Organic Liquids. By R. Varet (*Compt. rend.*, **114**, 224—225).—A comparison of the action of metals on salts dissolved in water and in various organic solvents has been made, with the view of determining the part played in the reaction by the water, and by the formation of molecular compounds among the products present.

1. Aluminium reacts with an aqueous solution of mercuric cyanide with the formation of alumina, hydrogen cyanide, hydrogen, and free mercury.

2. A solution of mercuric cyanide in (absolute) alcoholic ammonia yields with aluminium (in absence of all trace of water) a double cyanide of mercury and aluminium, combined with alcohol and ammonia. After treatment with aluminium in small pieces, the solution is filtered in a dry atmosphere, and the filtrate concentrated over a mixture of potash and quicklime; after several days, a thick, soft, transparent, crystalline layer of the complex compound of aluminium mercury cyanide with alcohol and ammonia separates out; it is so unstable that its composition cannot be ascertained with precision. In this reaction, the substitution of aluminium for mercury is never complete, as it only proceeds so far as the formation of the double cyanide.

3. If mercuric cyanide be dissolved in anhydrous pyridine, it does

not react with aluminium. If a small quantity of water be added, the reaction takes place as in 1, till the water is exhausted.

4. Nickel acts on a boiled aqueous solution of mercuric chloride with production of mercurous chloride and nickel chloride.

5. Mercuric chloride dissolved in pyridine is without action on nickel in the cold; when heated, substitution of the nickel occurs.

6. The same solution has no action on iron in the cold, or on heating. An immediate reaction occurs on adding water and heating slightly, with formation of calomel and oxidation of the iron.

The conclusion is drawn that certain metals, capable of precipitating others from their salts dissolved in water, lose this property when certain organic liquids are used as solvents, and that this difference is partly due to the water and partly due to the formation of molecular combinations between the products present.

W. T.

Polymeric Methylthiocarbimide. By A. W. v. Hofmann (*Ber.*, **25**, 876).—Methylthiocarbimide is polymerised when heated with potassium acetate, and by the action of phosphorus pentasulphide on methyl isocyanurate the thio-compounds intermediate between the latter and polymeric methylthiocarbimide are obtained, so that the following series of compounds is known:—$C_3O_3N_3Me_3$, $C_3O_2SN_3Me_3$, $C_3OS_2N_3Me_3$, and $C_3S_3N_3Me_3$. E. C. R.

Derivatives of Chromium Ammonium Thiocyanate. By O. T. Christensen (*J. pr. Chem.* [2], **45**, 213—222).—*Ammonium diaminechromiumthiocyanate*, $Cr(NH_3)_2(SCN)_3,NH_4{\cdot}SCN + H_2O$ (Reinecke's salt, *Annalen*, **126**, 113), is obtained, together with Morland's salt (this Journal, 1861, 252), when ammonium thiocyanate (200 grams) is melted in a porcelain crucible, and powdered potassium dichromate (40 grams) added by degrees; on treating the melt with cold water, the two salts crystallise out together as a red powder, and can be separated by washing with cold water, which dissolves Reinecke's salt; the latter crystallises out on the addition of a saturated solution of ammonium chloride. Morland's salt can be converted into Reinecke's salt by dissolving it in warm ammonia (sp. gr. 0·96), and adding a cold saturated solution of ammonium chloride to the hot liquid.

Reinecke's salt crystallises in rectangular tables; it is insoluble in absolute ether, but dissolves in water to a ruby-red solution and in alcohol. The colour of the salt on Radde's scale is purple 260. Those salts whose metals are precipitated by hydrogen sulphide in acid solution are also precipitated by ammonium diaminechromiumthiocyanate; the precipitates are insoluble in water, with the exception of that of cadmium, which dissolves with difficulty. Those salts whose metals are not precipitated by hydrogen sulphide in acid solution, but are precipitated by ammonium sulphide, give easily soluble precipitates with a concentrated solution of the thiocyanate. The alkali and alkaline earth metals give precipitates in saturated solutions of the thiocyanate. All these precipitates are described in the paper.

With solutions of the salts of most of the ordinary nitrogenous

organic bases, ammonium diaminechromiumthiocyanate gives precipitates consisting of compounds which contain the base in place of the NH_3 of the precipitant. Such compounds containing the alkaloïds are sparingly soluble. Several metallic ammonium derivatives, like the luteo- and purpureo-cobalt salts, are precipitated by the thiocyanate.

The reactions of Morland's salt are so similar to those of Reinecke's salt that the author regards the former as ammonium tetraminechromiumthiocyanate, $Cr(NH_3)_4(SCN)_3,NH_4SCN$. Hot water slowly decomposes Reinecke's salt and its derivatives. A saturated aqueous solution of the salt absorbs all the rays of the spectrum, with the exception of the red, from a little before C nearly up to D.

A. G. B.

Value of the Primary Alcoholic Function. By DE FORCRAND (*Compt. rend.*, **114**, 545—547).—The author extends to glycerol and erythritol the reasoning previously applied to glycol (this vol., p. 576), and shows that the primary alcoholic function has a constant thermal value of 32 Cal., when allowance is made for combination between the monometallic derivative and the excess of the alcohol or polyalcohol, which increases the apparent value of the primary alcoholic function, and for intramolecular combination between the metallic derivatives and the undisplaced hydroxyl groups, which lower the apparent values of the second, third, and fourth alcoholic functions.

C. H. B.

Preparation and Properties of Bunte's Salt (Sodium Ethylthiosulphate). By R. OTTO and A. RÖSSING (*Ber.*, **25**, 988—991).—Sodium ethylthiosulphate, $SEt{\cdot}SO_2{\cdot}ONa$, was first prepared by Bunte (this Journal, 1874, 770) by warming ethyl bromide with an aqueous solution of sodium thiosulphate, and later by Spring (this Journal, 1875, 129) by the action of iodine on a mixture of sodium ethylmercaptan and sodium sulphite. The authors have re-examined both methods, and find that in each case the yield is very small. In Bunte's reaction a considerable quantity of the salt decomposes even in aqueous solution with formation of ethyl bisulphide and sodium dithionate, a change which takes place quantitatively with the dry substance at 100°, as already shown by Bunte. A better yield may be obtained by heating the two compounds in very dilute alcohol at 80° for 2—3 days, allowing the solution to evaporate at the ordinary temperature, and extracting the residue with alcohol.

In Spring's reaction, the iodine largely acts on the two salts separately, and attempts to obtain sodium phenylthiosulphate by the same method led to similar results. Spring also states that the chloride of ethylthiosulphuric acid, prepared by the action of phosphorus pentachloride on the sodium salt, is resolved even in the cold into ethyl bisulphide, sulphurous anhydride, and sulphuryl chloride; the formation of the last-named compound has, however, been disputed by Ramsay (this Journal, 1875, 687), and the authors, on repetition of the experiments, have confirmed Ramsay's results.

H. G. C.

Fluorhydrins from Glycerol. By M. MESLANS (*Compt. rend.*, **114**, 763—766).—Bromine combines energetically with allyl fluoride,

forming a colourless liquid which boils at 162—163° without decomposition and without attacking the glass. No hydrogen fluoride is produced in the reaction. The liquid is *dibromofluorhydrin*, $C_3H_5Br_2F$; it is colourless and mobile, with an odour recalling that of chloroform, and a sweet, burning taste; sp. gr. at 18° = 2·09; vapour density 7·64.

Chlorine likewise combines with allyl fluoride, with development of heat and production of dichlorofluorhydrin, a colourless liquid similar in its properties to the bromine compound; it boils at 122—123°; sp. gr. at 18° = 1·327; vapour density 4·495.

Iodine has no action on allyl fluoride. Fluorine, even at a low temperature, decomposes allyl fluoride with formation of hydrogen fluoride and carbon fluoride, and separation of carbon. C. H. B.

Monosodium Mannitol. By de Forcrand (*Compt. rend.*, **114**, 226—228).—Monosodium mannitol has been prepared by adding finely-divided mannitol (1 mol.) to a solution of sodium ethoxide (1 mol.) in absolute alcohol (4 or 5 mols.), and boiling for 8—10 hours. It has the composition $C_6H_{13}NaO_6$. Its heat of solution in water (204 grams in 4 litres) is 4·86 Cal. at 11°. $C_6H_{14}O_6$ sol. + Na sol. = H gas + $C_6H_{13}NaO_6$ sol. + 34·82 Cal. Its heat of formation is represented by C_6 (diamond) + H_{13} gas + Na sol. + O_6 gas = $C_6H_{13}NaO_6$ sol. + 353·32 Cal. It crystallises with 4 mols. of ethyl alcohol. Attempts to prepare disodium mannitol in the same way resulted in the production of a compound of monosodium mannitol with sodium ethoxide which was stable at 150°. Its heat of formation is $C_6H_{13}NaO_6$ sol. + C_2H_5ONa sol. = $C_6H_{13}NaO_6,C_2H_5ONa$ sol. + 5·95 Cal. In general, the heat of formation of substances of this type is much less, about 1—2 Cal. As in the cases of glycol, glycerol, and erythrol, so with mannitol, we have—

1. The substitution of sodium for the first hydrogen atom in polyatomic alcohols results in a liberation of heat greater than +32 Cal.

2. The displacement of the second hydrogen atom liberates less than +32 Cal. W. T.

Rotatory Power of Compounds of Perseïtol with Sodium Hydrogen and Ammonium Hydrogen Molybdate. By D. Gernez (*Compt. rend.*, **114**, 480—482).—Perseïtol is slightly lævogyrate, but the compounds which it forms with molybdic acid and the alkaline hydrogen molybdates are strongly dextrogyrate, like the analogous compounds of mannitol and sorbitol previously described (Abstr., 1891, 1443; this vol., p. 422).

The molecular rotatory power of perseïtol in supersaturated aqueous solution (0·072 gram per c.c.) is $[\alpha]_D = -1° 12'$. The sign of the rotatory power is changed by the addition of even $\frac{1}{150}$ mol. of sodium hydrogen molybdate, and a maximum ($[\alpha]_D = +7° 11'$) is reached at a point at which the proportion of perseitol to molybdic acid (calculated as excess over that required to form the normal salt) is as 8 to 9. Almost identical results are obtained with the ammonium salt,

showing that the nature of the alkali has little influence on the optical activity of the compound. Jn. W.

Dextrose from Sulphite-cellulose and from Fir-wood. By T. B. Lindsey and B. Tollens (*Annalen*, **267**, 370—371).—The cellulose obtained by treating wood with calcium hydrogen sulphite dissolves in concentrated sulphuric acid, yielding a very dark solution; after adding water and boiling for a long time, and then proceeding in the usual manner, it is possible to isolate a small quantity of dextrose from the solution; 100 grams of the cellulose gave 3·5 grams of colourless sugar, from which, after recrystallisation, almost 2 grams of dextrose of specific rotatory power $[\alpha]_D = 52{\cdot}65°$ was obtained.

From 18 grams of crude fir-wood, the authors obtained 0·84 gram of dextrose of specific rotatory power $[\alpha]_D = 50{\cdot}4°$. F. S. K.

The Specific Rotatory Power of Cane Sugar in Dilute Solutions. By R. Nasini and V. Villavecchia (*Gazzetta*, **22**, i, 97—104). —The specific rotatory power of cane sugar in dilute solutions has been determined by various observers; the results obtained, however, are very inconsistent. The authors, working with pure cane sugar and using a Landolt-Lippich polaristrobometer with a column of the active liquid about half a metre long, have obtained the following results at 20°:—

Percentage of sugar.	$[\alpha]_D$ observed.	$[\alpha]_D$ calculated.	Percentage of sugar.	$[\alpha]_D$. observed.	$[\alpha]_D$ calculated.
1·2526	66·604	66·783	0·6626	67·370	67·552
1·2191	66·719	66·792	0·5982	67·562	67·715
1·2048	66·855	66·785	0·5877	67·983	67 744
0·9926	67·096	66·963	0·3351	68·241	68·539
0·8243	67·250	67·213	—	—	—

In the table, the first column gives the percentage (p) of sugar present in the aqueous solution, and the second column shows the corresponding specific rotatory powers. The observed rotatory powers can be only approximately expressed as a function of the concentration by an equation containing three constants. The rotatory powers given in the third column are calculated from the equation

$$[\alpha]_D = 69{\cdot}962 - 4{\cdot}8696p + 1{\cdot}86145p^2.$$

The results obtained by the authors do not agree with those of Tollens (Abstr., 1884, 1285) and Pribram (Abstr., 1887, 755).

W. J. P.

Combination of Starch with Iodine. By G. Rouvier (*Compt. rend.*, **114**, 749—750).—According to Mylius, starch only combines with iodine when hydriodic acid or an iodide is also present in the proportion of 1 mol. of the acid or the iodide to 4 atoms of iodine.

The author finds, however, that iodine and starch readily combine in presence of alcohol, when the amount of iodine present in the form of an iodide is not more than 3 per cent. of the total quantity of the iodine. C. H. B.

Wood Sulphite-liquor and Lignin. By J. B. Lindsey and B. Tollens (*Annalen*, **267**, 341—366).—The liquid obtained in the preparation of cellulose for paper making, by heating wood with calcium hydrogen sulphite, gives 9·46 per cent. of residue on evaporation at 100°. When heated with hydrochloric acid, it yields only a small quantity of levulinic acid, a fact which proves the absence of hexoses in any considerable quantity. The absence of dextrose, and of compounds which yield dextrose, is proved by the fact that saccharic acid cannot be isolated from the products of the oxidation of the liquor with nitric acid; galactose, or a derivative of this sugar, on the other hand, is present in the liquor in not inconsiderable quantities, as is shown by the formation of mucic acid. The presence of mannose is proved by the fact that it can be isolated in the form of its hydrazone. The liquor also contains small quantities of pentoses, or of derivatives thereof, as it gives furfuraldehyde on distillation with hydrochloric acid; there is also present in the liquor a trace of vanillin or of a substance having very similar properties. When the liquor is freed from sulphurous acid and then treated with yeast under suitable conditions, fermentation sets in, and a small quantity of alcohol is produced.

When wood sulphite-liquor is freed from sulphuric acid with the aid of barium hydroxide, and then treated with a solution of lead acetate, there is produced a precipitate which contains, in addition to sulphur and other inorganic matter, an organic substance of the composition $C_{26}H_{32}O_{12}$ or $C_{26}H_{30}O_{12}$; this precipitate, on decomposition with dilute sulphuric acid, yields a dark solution, from which, after evaporating to a syrup, a grey, flocculent substance is deposited on the addition of alcohol. Analyses, and methoxy-determinations by Zeisel's method, made with samples of this flocculent substance, and calculated for the ash-free sample, gave results agreeing well, except in the case of the sulphur, with those required by a compound of the composition $C_{24}H_{24}Me_2SO_{12}$. The filtrate from the flocculent precipitate gives, on evaporation at 100°, a dark powder, which is readily soluble in water, and which reduces Fehling's solution; analyses of this product, which contained 3·4 per cent. of ash, gave results from which the composition of the organic matter was calculated to be $C_{24}H_{24}Me_2SO_{12} + 1\frac{1}{2}H_2O$.

A colourless, flocculent precipitate is produced when wood sulphite-liquor is mixed with an equal volume of hydrochloric acid of sp. gr. 1·19; this precipitate, after having been washed with concentrated hydrochloric acid and dried over sulphuric acid, contains 1·99 per cent. of ash; the composition of the ash-free substance can be expressed by the formula $C_{26}H_{30}SO_{10}$. The acid filtrate from this flocculent compound gives, with bromine, an amorphous precipitate which, when dried over sulphuric acid, is obtained in the form of a yellowish-brown powder containing 1·32 per cent. of ash; analyses of this

product, calculated for the ash-free sample, gave results agreeing with those required by a compound of the composition $C_{26}H_{28}Br_4SO_{11}$.

As all the substances described above could only be obtained in an amorphous condition, it is possible that they may be mixtures; if, as is probable, the sulphur is present, in part, at any rate, in the form of a sulphonic acid group, the composition $C_{26}H_{30}O_{10}$ may be assigned to the substance, or substances, from which the above sulphur compounds are formed. The composition $C_{26}H_{30}O_{12}$ is approximately the same as that assigned by Dietrich and König to lignin, and agrees also moderately well with that given to lignon, the lignin of jute, by Cross and Bevan (Trans., 1889, 213); the composition $C_{26}H_{30}O_{10}$ agrees very closely with that assigned by Lange to lignic acid.

The behaviour of the compound obtained from wood sulphite-liquor resembles, in some respects, that of the tannic acids, but the characteristic reaction of these acids with ferric salts is not given by the compound in question; if, as quite recent experiments seem to show, the sulphur in this compound is really present in the form of a sulphonic acid group, it would resemble rather the substances obtained by Schiff (*Annalen*, **178**, 171) by the action of sulphuric acid on monhydric and polyhydric phenols. F. S. K.

Vegetable Amyloïd. By E. Winterstein (*Ber.*, **25**, 1237—1241).—The substance described under the name "amyloïd" is a constituent of the cell walls of certain plants, and gives the same coloration with iodine as starch does. According to Reiss (*Landw. Jahrb.*, **18**, 733), on hydrolysis with dilute sulphuric acid, it yields considerable quantities of glucose, but as the material used by him also contained cellulose, this statement is open to the objection that the latter was the source from which the glucose was obtained. The author has therefore prepared pure samples of amyloïd, and examined its behaviour on hydrolysis, with results very different from those obtained by Reiss.

To prepare the amyloïd, the seeds of *Tropæolum majus* were extracted successively with ether, cold alcohol, dilute ammonia, dilute soda, and cold water; the residue was boiled with water, filtered, and the solution precipitated with alcohol. The amyloïd separates as a jelly, and is purified by redissolving in water and again precipitating with alcohol. It then forms a colourless, transparent jelly, which dries in the desiccator to an amorphous, vesicular mass, and is coloured blue by starch, the colour disappearing on warming. Its aqueous solution is dextrorotatory ($[\alpha]_D = 93{\cdot}5^\circ$), and it is not converted into sugars by diastase; on oxidation with nitric acid, it yields mucic acid, and with hydrochloric acid gives 15·44 per cent. of furfuraldehyde. On hydrolysis with 2·5 per cent. sulphuric acid, it yields galactose, together with a smaller quantity of another hexose of lower dextrorotatory power, and a pentose which yields trihydroxyglutaric acid on oxidation, and is therefore probably xylose, the second hexose being probably glucose. If the residue, after extracting the seeds with hot water, be boiled with 3 per cent. sulphuric acid, it yields further quantities of galactose and xylose.

The author, therefore, regards amyloïd as a substance corresponding

somewhat with starch or cellulose, but derived from galactose and xylose, instead of from glucose. Whether the substance is really homogeneous is not yet certain, but the fact that the amyloïd prepared from the seeds of *Pæonia officinalis* yields almost the same quantities of mucic acid and furfuraldehyde is in favour of this supposition. H. G. C.

Propylamines and their Derivatives. By F. Chancel (*Compt. rend.*, **114**, 756—758).—When ethyl oxalate is added gradually to a well cooled mixture of equal volumes of monopropylamine and water, a considerable proportion of propyl oxamate and monopropylamine oxalate is formed. When the dipropyloxamide is filtered off and calcium chloride is added to the filtrate, calcium oxalate is precipitated and calcium propyloxamate remains in solution, but separates when the liquid cools. Propyloxamic acid is obtained by decomposing the calcium salt with hydrochloric acid and extracting with ether. It crystallises in long, white needles, very soluble in water, alcohol, and ether; it melts at 109—110°, and sublimes at about the same temperature. Its calcium salt crystallises in small, brilliant prisms with 2 mols. H_2O, when its solution is slowly cooled. If the solution is cooled rapidly, long filaments separate which contain 3 mols. H_2O, but readily lose one of them.

Propylamidoacetic acid is readily obtained by heating monopropylamine with ethyl bromacetate at 100—110°. It is purified by conversion into the copper salt, which is recrystallised and then decomposed by hydrogen sulphide. From alcohol it crystallises in needles. It sublimes easily, and is very readily soluble in water or alcohol, but insoluble in ether. Its platinochloride crystallises in prisms with 1 mol. H_2O, and is very soluble in water. The aurochloride could not be obtained. The copper salt is very soluble in water or alcohol, and crystallises in nodules or crusts.

C. H. B

Action of Sodium and Potassium Cyanide on Chlorodiamylamine. By A. Berg (*Compt. rend.*, **114**, 483—486).—*Amylamylenamine*, $C_5H_{11}{\cdot}N{:}C_5H_{10}$, is prepared by treating chlorodiamylamine (1 mol.) with alcoholic soda (1 mol.). Sodium chloride first separates, and the reaction is completed by heating in a reflux apparatus. The alcohol is distilled off, the salt dissolved out with water, and the crude, oily residue dried over potash, and redistilled. The product thus obtained is not pure, however, but a mixture of the amylamylenamine with unchanged diamylamine, the boiling points of which are too near to admit of fractionation. The presence of the former base is shown by the formation of valeraldehyde and amylamine when the mixture is hydrolysed with hydrochloric acid, and the pure base is readily prepared from these substances by simply heating them together in molecular proportions. It is a colourless liquid, which boils at 180—181° under a pressure of 764 mm. It combines with methyl iodide in the cold, and restores the colour to rosaniline which has been decolorised with sulphurous acid.

Diamylcyanamide, $CN{\cdot}N(C_5H_{11})_2$, is prepared by heating alcoholic rodiamylamine (1 mol.) with aqueous potassium cyanide (1 mol.

in minimum quantity of water) in a reflux apparatus for several hours. The alcohol is distilled off, the residue washed with water and dilute sulphuric acid, and then redistilled under diminished pressure. Diamylcyanamide, as thus prepared, is a light, viscous, colourless liquid, which boils at 143—144° under a pressure of 20 mm., dissolves in cold, concentrated hydrochloric acid, and is reprecipitated by water. It is hydrolysed by concentrated hydrochloric acid at 160° into diamylamine, carbonic anhydride, and ammonia. Jn. W.

Preparation of Pure Trimethylamine from Crude Trimethylamine Hydrochloride. By E. Schmidt (*Annalen*, **267**, 254—268).—For the preparation of pure trimethylamine from the commercial hydrochloride, which contains as impurities the hydrochlorides of mono- and di-methylamine, ammonium chloride, and seemingly, also, small quantities of the hydrochlorides of amines richer in carbon, the following method was found, after many experiments, to be the most satisfactory. The crude trimethylamine hydrochloride (250 grams) is placed in a flask of 2 litres capacity, excess of concentrated soda gradually added with the aid of a funnel, and the mixture finally heated to expel the whole of the base; the impure trimethylamine is passed first through a reflux condenser, then through a potash tower, and is finally collected in two wash-bottles, each containing 150 grams of alcohol, and well cooled during the operation. Methyl bromide is then passed into the well-cooled alcoholic solution until the latter no longer shows an alkaline reaction, and the precipitated tetramethylammonium bromide is separated by filtration, washed with alcohol, and dried; this crystalline compound is converted into the corresponding hydroxide by treating it with moist silver oxide in the usual manner, and the anhydrous, crystalline tetramethylammonium hydroxide is then gradually heated in a large flask in a slow stream of hydrogen. The mixed vapours of methyl alcohol and trimethylamine are passed through two condensers, when the former is liquefied and collected in a flask, and the pure trimethylamine, after passing through a potash tower, is finally collected in alcohol. F. S. K.

Action of Isobutyl Iodide on Trimethylamine. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **6**, 709—711).—A mixture of isobutyl iodide and trimethylamine in molecular proportion is heated with water in sealed tubes at 100° for three days. In addition to trimethylisobutylammonium iodide, which affords a stable platinochloride $(NMe_3{\cdot}C_4H_9)_2,PtCl_6$, a small quantity of butylene is produced. The same products are obtained when the above mixture is frequently agitated during three months in the cold, and the authors think the butylene results from the action of hydrogen iodide on tertiary isobutyl iodide existing as an impurity in the alkyl iodide used.

T. G. N.

Action of Isoamyl Iodide on Trimethylamine. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **6**, 711).—A mixture of isoamyl iodide with trimethylamine in molecular proportion reacts in the cold when well shaken in presence of water in sealed tubes for six days.

On evaporating the product, white, nacreous crystals of trimethylisoamylammonium iodide are obtained, which yield a platinochloride, $(NMe_3{\cdot}C_5H_{11})_2PtCl_6$. The chemical activity of isoamyl iodide and of tri-isoamyline in respect to amines and alkyl iodides respectively is greater than that of the corresponding butyl derivatives.

T. G. N.

Action of Capryl Iodide on Trimethylamine. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **6**, 845).—A mixture of capryl iodide with trimethylamine in molecular proportion is heated with water in sealed tubes for successive periods of 48 hours at 100° and 155°. The lower of the two layers contains tetramethylammonium iodide, which crystallises out, and some trimethylamine iodide, and in the supernatant layer dimethylamine and some caprylene occur.

T. G. N.

Derivatives of Neurine and Choline. By J. Bode (*Annalen*, **267**, 268—299).—Trimethylamine ethylene bromide, $NMe_3Br{\cdot}C_2H_4Br$, prepared according to Hofmann's method, by treating the base with ethylene bromide in alcoholic solution, crystallises from alcohol in lustrous plates melting at 230°, and from cold water in large, monoclinic plates, $a : b : c = 0{\cdot}8478 : 1 : 0{\cdot}86958$, $\beta = 71° 2' 7''$; on prolonged boiling with an aqueous solution of silver nitrate (2 mols.) it is converted into trimethylethoxyammonium hydroxide (choline). When treated with excess of bromine in alcoholic solution, a perbromide of the composition $NMe_3Br{\cdot}C_2H_4Br,Br_2$ is deposited in golden crystals melting at 147—148°; this compound is insoluble in cold, and is decomposed by boiling alcohol and by boiling water.

Trimethylvinylammonium bromide, $NMe_3Br{\cdot}C_2H_3$, can be obtained by treating trimethylamine ethylene bromide with silver oxide and then saturating the filtered solution with hydrogen bromide; it is a colourless, very hygroscopic compound, melts at 193°, and is readily soluble in water and alcohol, but insoluble in ether. The corresponding *iodide*, $NMe_3I{\cdot}C_2H_3$, prepared in like manner, crystallises from hot alcohol in colourless needles, turns yellow at about 180°, melts at 196°, and is readily soluble in water and hot alcohol.

Dibromethyltrimethylammonium bromide, $NMe_3Br{\cdot}CHBr{\cdot}CH_2Br$, is formed when bromine is added to an alcoholic solution of trimethylvinylammonium bromide, or of the corresponding chloride; it crystallises from hot alcohol in colourless needles, and from cold water in plates, turns brown when heated, and melts at 165°; it combines with bromine, yielding a crystalline, unstable perbromide,

$$NMe_3Br{\cdot}C_2H_3Br_2,Br_2,$$

which melts at 73°.

Dibromethyltrimethylammonium chloride, $NMe_3Cl{\cdot}CHBr{\cdot}CH_2Br$, can be obtained by treating a cold aqueous solution of the corresponding bromide with excess of silver chloride; it separates from alcoholic ether in colourless needles, and is very readily soluble in water, but rather more sparingly in alcohol. The *platinochloride*,

$$(C_5H_{12}NBr_2Cl)_2,PtCl_4,$$

crystallises from hot, dilute hydrochloric acid in orange needles,

melts at 220°, and is only sparingly soluble in cold water. The *aurochloride*, $C_5H_{12}NBr_2Cl,AuCl_3$, crystallises in golden plates, melts at 216°, and is only sparingly soluble in cold, but more readily in hot water.

Bromovinyltrimethylammonium bromide, $NMe_3Br{\cdot}CH{:}CHBr$, is formed when dibromethyltrimethylammonium bromide is treated with alcoholic potash (1 mol.); it separates from alcoholic ether in colourless, lustrous plates, melts at 146—147°, and dissolves freely in alcohol and water. The *aurochloride*, $C_5H_{11}NBrCl,AuCl_3$, crystallises from dilute hydrochloric acid in golden prisms melting at 223°. The *platinochloride*, $(C_5H_{11}NBrCl)_2,PtCl_4$, forms well-defined prisms and melts at 202°.

Tribromethyltrimethylammonium bromide, $NMe_3Br{\cdot}CHBr{\cdot}CHBr_2$, can be prepared by treating the preceding compound with bromine in chloroform solution; it crystallises from hot alcohol in colourless needles, melts at 152°, and is readily soluble in water and hot alcohol.

Acetenyltrimethylammonium platinochloride, $(NMe_3Cl{\cdot}C{:}CH)_2,PtCl_4$, is precipitated when bromovinyltrimethylammonium bromide is treated with alcoholic potash (2 mols.), the filtered solution acidified with hydrochloric acid, and then mixed with platinic chloride; it separates from dilute hydrochloric acid in orange crystals, melts at 218° after previously turning brown, and is readily soluble in water. The corresponding *aurochloride*, $NMe_3Cl{\cdot}C{:}CH,AuCl_3$, crystallises in golden needles, melts at 245°, and is only sparingly soluble in cold water. When a solution of the corresponding chloride is treated with bromine, there is formed a *bromo*-derivative of the composition $NMe_3Br{\cdot}C_2HBr_4$; this substance separates from alcoholic ether in colourless crystals melting at 146°. The physiological action of the acetenyl base has been examined by Schmidt (compare this vol., p. 905).

Chlorethoxytrimethylammonium platinochloride,

$$(NMe_3Cl{\cdot}C_2H_3Cl{\cdot}OH)_2,PtCl_4,$$

is obtained when trimethylvinylammonium chloride is treated with hypochlorous acid, the alcoholic solution of the product acidified with hydrochloric acid, and mixed with platinic chloride; it separates from dilute hydrochloric acid in long, orange, prismatic crystals melting at 205—207°.

Trimethylchlorethylammonium platinochloride,

$$(NMe_3Cl{\cdot}C_2H_4Cl)_2,PtCl_4,$$

can be prepared by decomposing the platinochloride just described with hydrogen sulphide, treating the hot solution of the product with tin and hydrochloric acid, and, after precipitating the tin, adding a solution of platinic chloride; it separates from dilute hydrochloric acid in small, yellow, octahedral crystals, melts at 260°, and is only very sparingly soluble in cold water.

Trimethyldihydroxyethylammonium platinochloride,

$$[NMe_3Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}OH]_2,PtCl_4,$$

is obtained when chlorethoxytrimethylammonium chloride is treated with moist silver oxide, and the hydrochloric acid solution of the product precipitated with platinic chloride; it forms small, yellow crystals, melts at 264°, and is only sparingly soluble in cold water.

The *aurochloride*, $NMe_3Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,AuCl_3$, crystallises in long, golden needles, melts at 237°, and is only sparingly soluble in cold water. The physiological action of trimethyldihydroxyethyl ammonium chloride (isomuscarine chloride, or hydroxycholine chloride) has been previously referred to (compare Schmidt, *loc. cit.*).

A compound of the composition $NMe_3,C_8H_8Br_2$ is deposited in colourless, nodular crystals when a 33 per cent. alcoholic solution of trimethylamine is warmed with cinnamene dibromide at 50—60°; it crystallises from alcoholic ether in colourless plates, melts at 202°, and is very readily soluble in water, and moderately easily in alcohol; on keeping, it decomposes with liberation of trimethylamine.

F. S. K.

Action of Hydriodic and of Hydrobromic Acid on Neurine and Choline. By E. Schmidt (*Annalen*, **267**, 300—318).—*Trimethylamine ethylene iodide*, $NMe_3I{\cdot}CH_2{\cdot}CH_2I$, is formed when neurine iodide is heated with concentrated hydriodic acid at 100° for several hours; it separates from hot water in colourless crystals, melts at 230—231°, and is only very sparingly soluble in boiling alcohol; when heated for a long time with a slight excess of silver nitrate in aqueous solution, it yields choline and only a very small quantity of neurine.

The *platinochloride* of β-iodethyltrimethylammonium chloride, $(NMe_3Cl{\cdot}C_2H_4I)_2,PtCl_4$, is obtained when a cold aqueous solution of the preceding compound is digested with silver chloride, the filtrate acidified with hydrochloric acid, and treated with platinic chloride; it separates from hot dilute hydrochloric acid in small, orange-yellow crystals, melts at 234° with decomposition, and is only very sparingly soluble in cold water. The corresponding *aurochloride*,

$$NMe_3Cl{\cdot}C_2H_4I,AuCl_3,$$

forms lustrous, golden plates, melts at 193·5° with decomposition, and is very sparingly soluble in cold water.

The trimethylamine ethylene iodide (β-iodethyltrimethylammonium iodide) prepared from neurine is identical with the compound obtained by Baeyer (*Annalen*, **140**, 306) by heating neurine hydrochloride (choline chloride) with hydriodic acid. The same compound is formed, but only in small quantities, when an alcoholic solution of trimethylamine is heated at 50° with ethylene iodide; when an aqueous solution of the compound is treated with moist silver oxide, the filtered solution acidified with hydrochloric acid and mixed with platinic chloride, neurine platinochloride is precipitated; it is possible, therefore, to convert choline into neurine, and *vice versâ*, in a comparatively simple manner.

When neurine iodide is heated for six hours at 100° with concentrated hydrobromic acid, it seems to give a mixture of trimethylamine ethylene bromide (compare this vol., p. 806) and trimethylamine ethylidene bromide, in which the former is present in the larger quantity; when this mixture is treated with silver nitrate in aqueous solution, choline and smaller quantities of neurine are obtained.

F. S K.

Formation of Bromaldehydes and Bromoketones by the Action of Bromine on Alcohols of the Ethyl Series. By A. Étard (*Compt. rend.*, **114**, 753—755).—The author is unable to confirm the usual statement that the action of bromine on normal propyl alcohol yields propyl bromal. The action of 1 mol. of bromine (Br_2) on 1 mol. of propyl alcohol develops a considerable quantity of heat, but the liquid afterwards requires to be heated in order to make the reaction complete. Dibromopropaldehyde, $C_3H_4Br_2O$, is formed together with propyl bromide and some propyl bromopropionate.

Dibromopropaldehyde obtained in this way is a colourless liquid which boils without decomposition at 137°; sp. gr. at 15° = 1·899. Its vapour is intensely irritating to the eyes. It combines with sodium hydrogen sulphite to form a compound crystallising in nacreous scales, and with water it forms a very soluble hydrate, $C_3H_4Br_2O + 2H_2O$, which crystallises in beautiful prisms. The constitution of the derivative is, probably, $CMeBr_2{\cdot}COH$.

Isopropyl alcohol, under the same conditions, is very rapidly attacked by bromine, and yields isopropyl bromide boiling at 61°, and acetyl bromoform, $COMe{\cdot}CBr_3$, which forms phenylcarbylamine in presence of aniline, and yields bromoform when treated with ammonia. Acetyl bromoform boils, with decomposition, at 255°, and unites with difficulty with hydrogen sulphites.

Normal butyl alcohol is not readily attacked by bromine; it yields monobrombutaldehyde, boiling at 235°.

Isobutyl alcohol is attacked more easily; the products are isobutyl bromide, isobutyl isobutyrate, and bromisobutaldehyde. The latter boils at 197° with some decomposition.

Trimethylcarbinol explodes feebly in contact with bromine, and isobutylene bromide, $CMe_2Br{\cdot}CH_2Br$, boiling at 148°, is formed.

Fermentation amyl alcohol reacts readily with bromine, and yields amyl bromide, bromovaleral boiling at 125° under a pressure of 80 mm., dibromovaleral, and dibromovaleraldehyde, which boils at 155—160° under a pressure of 80 mm., and oxidises to dibromovaleric acid when exposed to the air.

The amyl alcohol $OH{\cdot}CMe_2{\cdot}CH_2Me$, when treated with bromine, loses water and yields amylene dibromide, $CMe_2Br{\cdot}CHBrMe$, boiling at 172°.

When bromine acts on isobutyl and amyl alcohols in presence of an alkali, it produces carbon tetrabromide and alkaline butyrates or valerates. C. H. B.

Preparation of Crotonaldehyde. By J. A. Müller (*Bull. Soc. Chim.* [3], **6**, 795—796).—Crotonaldehyde is best prepared by heating 100 grams of acetaldehyde with 0·7 c.c. of zinc chloride solution (containing 150 grams per 100 c.c.), in sealed tubes at 100° for 48 hours. The product is distilled on a water-bath, and the residue, after treatment with saturated sodium carbonate solution, is filtered, dehydrated by potassium carbonate, and subjected to repeated fractionations from fused calcium chloride in an atmosphere of carbonic anhydride. A yield amounting to 16·7 per cent. of the acetaldehyde actually used is obtained. T. G. N.

Occurrence of a Tetracarbon Aldehyde in a Brandy. By J. A. Muller (*Bull. Soc. Chim.* [3], **6**, 796—800).—A badly tasting brandy, distilled from a "piquette" wine resulting from the fermentation of grape marc washings yielded, on treatment with moist silver hydroxide, silver γ-oxybutyrate, from which the corresponding calcium and barium salts were prepared. A further portion of the spirit afforded a yellow, oily oxime, C_4H_7NO, which probably results from the presence therein of an isocrotonaldehyde, $CH_2{:}CH{\cdot}CH_2{\cdot}CHO$.

T. G. N.

Action of Chlorine on some Fatty Ketones. By Démètre-Vladesco (*Bull. Soc. Chim.* [3], **6**, 807—836; compare Abstr., 1890, 956; 1891, 1183; this vol., 424).—Chlorethyl methyl ketone, when heated with water in sealed tubes at 150° for eight hours, affords *methylacetylcarbinol*, which boils at 140—150°. Sodium reacts on a dry ethereal solution of the chloroketone to yield a liquid diketone, $(COMe{\cdot}CHMe)_2$, soluble in ether and in alcohol, boiling at 210°, and forming crystalline compounds with phenylhydrazine and sodium hydrogen sulphite. Chlorethyl methyl ketone and sodium (equal mols.) react in alcoholic solution, yielding a ketonic alcohol, $C_4H_8O_2$, which boils at 140—145°, and reduces cold Fehling's solution and warm ammoniacal argentic nitrate. It dissolves in the ordinary solvents and combines with phenylhydrazine to yield a diacetylosazone (m. p. 2·420) identical with that obtained by v. Pechmann (Abstr., 1891, 738).

Potassium acetate and chlorethyl methyl ketone, when heated at 150° for 12 hours, afford *methylacetylcarbinyl acetate*, CHMeAc·OAc, an acetous liquid boiling at 160° under a pressure of 760 mm., which is but slightly soluble in the ordinary solvents. It combines with phenylhydrazine, and by the action of potassium hydroxide affords methylethylcarbinol. By this general reaction, the author prepared *methylacetylcarbinyl butyrate*. Alcoholic solutions of the chloroketone and potassium cyanide (equal mols.) are heated in sealed tubes at 120° for three hours, and a liquid ketonic nitrile, *methylacetylacetonitrile*, CN·CHMe·COMe, is formed, which boils at 156° under a pressure of 755 mm., and is a lower homologue of the compound obtained by Hanriot and Bouveault (Abstr., 1889, 841). This compound is insoluble in water, but dissolves in the ordinary solvents, and has a sp. gr. at 0° of 0·9934 and a vapour density of 3·35. With ammoniacal silver nitrate solution, it forms a crystalline compound CN·CMeAg·COMe, and on treatment with potassium hydroxide, it evolves ammonia, a potassium salt, COMe·CHMe·COOH, being formed; this is decomposed by sulphuric acid with formation of carbonic anhydride and methyl ethyl ketone, and when heated with ethyl iodide and alcohol in sealed tubes at 150° yields ethyl methylacetoacetate. The nitrile itself forms a yellow, oily compound with phenylhydrazine, $C_{11}H_{13}N_3$, which distils at 305—315°, and is, perhaps, by a molecular transformation converted into phenyldimethylamidopyrazole [1 : 3 : 4 : 5], as in the case of the β-ketonic nitriles (Bouveault, Abstr., 1891, 51).

Chlorethyl methyl ketone reacts in the cold with a solution of sodium in phenol, and the oily, insoluble product, after washing with alkaline hydroxide solution and drying over potassium carbonate, affords on fractionation at 235—240°, *αα-acetylphenoxyethane*, OH·CMePh·COMe, which is insoluble in water, but dissolves in the ordinary solvents, and on treatment with dilute sulphuric acid loses a molecule of water, and forms *αβ*-dimethylcoumarone, which distils at 260°.

The author was unable to isolate an amido-ketone from the product of the action of ammonia gas on an alcoholic solution of chlorethyl methyl ketone, but evaporation of the alcoholic solution affords a viscid liquid from which hot water extracts long needles of tetramethylpyrazole, $C_8H_{12}N_2$, melting at 86°; the constitution and formation of the pyrazoles is discussed, and in this case the author thinks it results from a condensation of 2 mols. of the amidoethyl methyl ketone with subsequent elimination of a molecule of water and of hydrogen.

Chlorethyl methyl ketone combines with aniline at 100°, and with methylaniline at 200°, to yield 2′ : 3′-dimethylindole and 1′ : 2′ : 3′-trimethylindole respectively (Abstr., 1890, 1421).

Chlorethyl methyl ketone forms crystalline compounds with trimethylamine, with dimethylamine, and with carbamide. Sodium ethoxide reacts with it to yield an ether-like compound, but the investigation of these substances is incomplete owing to the death of the author. The chlorination of methyl propyl ketone, diethyl ketone, and dipropyl ketone afforded similarly constituted monochloroketones, boiling at 130—133°, 145°, and 167° respectively, and which, so far as they were investigated, more especially in respect to the formation of pyrazoles, gave reactions similar to those of chlorethyl methyl ketone. T. G. N.

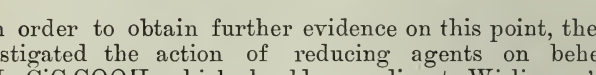
Chlorinated Diacetylacetone. By F. Feist (*Ber.*, **25**, 1067—1070).—When dehydracetic chloride is heated with water for several hours at 200°, a gas is evolved, and a small quantity of dehydracetic acid is formed; the principal product is, however, a crystalline compound, which melts at 83—85°, and is identical with the substance obtained by Collie (Trans., 1891, 619) by boiling dehydracetic acid with concentrated hydrochloric acid. The compound in question has the composition $C_7H_9O_2Cl + 2H_2O$, not $C_7H_{11}O_3Cl$, as stated by Collie, and is hydrochlorodimethylpyrone containing water of crystallisation; it loses 2 mols. H_2O over sulphuric acid under reduced pressure, the anhydrous substance being very hygroscopic, and melting at 154°. F. S. K.

Dry Distillation of Silver Salts of Organic Acids. By A. Lieben (*Ber.*, **25**, 1188—1189).—The author points out that the results obtained by Kachler (this vol., p. 37) have been previously obtained by Iwig and Hecht (Abstr., 1886, 439). He also discusses the observations of Koenig's (this vol., p. 293) in relation to those of Kachler. E. C. R.

Stereoisomerism of Oleïc and Elaïdic Acids. By A. Saytzeff (*J. pr. Chem.* [2], **45**, 300—302).—This is a preliminary notice. An isoerucic acid has been isolated (compare Abstr., 1888, 815).

A. G. B.

Stereometric Relations of Erucic Acid and Brassidic Acid. By A. Holt (*Ber.*, **25**, 961—965).—In a previous paper (this vol., p. 429), the author has shown that the relations between erucic acid and brassidic acid are best explained by the stereometric formulæ:—



Erucic acid. Brassidic acid.

In order to obtain further evidence on this point, the author has investigated the action of reducing agents on behenolic acid, $C_{19}H_{39}\cdot C{:}C\cdot COOH$, which should, according to Wislicenus' hypothesis, yield as first product an acid having the stereometric formula above assigned to brassidic acid, and which should therefore, if the author's views are correct, be identical with that acid. The results obtained show that brassidic acid is formed without any admixture of erucic acid.

Alkaline reducing agents are without action on behenolic acid, but it is readily attacked by zinc dust and acetic acid if a few drops of hydrochloric acid be added to the liquid. The product is pure brassidic acid, and combines with bromine forming the known dibromide. It was also found that zinc and acetic acid do not convert erucic acid into brassidic acid, and the latter must therefore be regarded as the sole product of the action of reducing agents on behenolic acid.

Hydrobromic acid saturated at 0° also acts on behenolic acid at 100° with formation of bromobrassidic acid, which, on reduction with sodium in alcoholic solution, yields brassidic acid. The action of hydrochloric acid does not proceed so smoothly, a hydroxy-acid, $OH\cdot C_{22}H_{41}O_2$, being obtained together with oily substances; the acid melts at 80°, and forms a heavy, crystalline silver salt, stable towards light.

The dibrom-additive product of behenolic acid (dibromobrassidic acid) and also di-iodobrassidic acid, when treated with sodium in alcoholic solution, re-form behenolic acid; the tetrabromide of behenolic acid behaves in the same manner, and does not, as stated by Haussknecht (*Annalen*, **143**, 40), yield erucic acid.

For the preparation of behenolic acid, the author employs a modification of v. Grossmann's method (*Inaug. Diss., Leipsic*, 1890), which consists in boiling 1 part of the dibromide of erucic acid with 2 parts of potash and 8—9 parts of 96 per cent. alcohol. The yield is 80 per cent. of the theoretical.

H. G. C.

Lactonic Acids, Lactones, and Unsaturated Acids. By R. Fittig (*Annalen*, **267**, 186—191).—General remarks on the papers by Fittig and Ström (next abstract), and by Fittig and Parker (this vol., p. 814).

F. S. K.

Action of Sodium Ethoxide on Butyrolactone. By R. Fittig and K. T. Ström (*Annalen*, **267**, 191—203; compare Abstr., 1890, 866—869). — *Dibutolactone*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2-O\end{matrix}>C:C<\begin{matrix}CO\cdot O\\ |\\ CH_2\cdot CH_2\end{matrix}$, is formed, together with γ-ethoxybutyric acid (see below), when butyrolactone (1 mol.), prepared by the method described by Chanlaroff (*Annalen*, **226**, 325), is heated on the water-bath for about three hours with an alcoholic solution of sodium ethoxide (1 mol.); after distilling off the alcohol, the residue is washed with ether, dissolved in water, the ice-cold solution mixed with 15 per cent. hydrochloric acid, and the products then extracted by repeatedly shaking with ether; the acid is separated from the lactone by agitating the ethereal extract with soda. Dibutolactone separates from hot ether in small, rosette-like aggregates, and from water in larger, scaly crystals; it melts and turns slightly yellow at 86·5°, and is readily soluble in chloroform, hot water, benzene, and alcohol, but only sparingly in carbon bisulphide and cold ether.

Oxetonecarboxylic acid, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2-O\end{matrix}>C<\begin{matrix}CH(COOH)\cdot CH_2\\ |\\ O\text{———}CH_2\end{matrix}$, is precipitated when concentrated soda is gradually added to dibutolactone, suspended in a small quantity of warm water, and the solution then acidified. It crystallises from cold water in needles, melts at 156°, and is readily soluble in alcohol and moderately easily in hot water, but only sparingly in cold ether and chloroform, and insoluble in carbon bisulphide. The *calcium* salt, $(C_8H_{11}O_4)_2Ca$, and the *barium* salt, $(C_8H_{11}O_4)_2Ba$, are colourless, amorphous compounds, readily soluble in water, but more sparingly in alcohol. The *silver* salt, $C_8H_{11}O_4Ag$, crystallises from warm water in small needles, is only moderately stable in the light, and is decomposed by boiling water, with separation of silver and carbonic anhydride and formation of oxetone.

Oxetone, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2-O\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ |\\ O-CH_2\end{matrix}$, is formed when its carboxylic acid is heated above its melting point, or is boiled with water or dilute mineral acids; it is most easily prepared by boiling dibutolactone with dilute acids. It is a colourless, mobile, highly refractive liquid, specifically lighter than water, and readily volatile with steam; it has a strong, peppermint-like odour, boils at 159·4°, and is soluble in 10 to 15 parts of water at the ordinary temperature, the solution becoming turbid when treated with potassium carbonate, or when gently warmed, but clear again when heated at about 90°; it is miscible with alcohol, ether, chloroform, and benzene in all proportions. It is not acted on by boiling dilute acids, or by alkalis, but it immediately reduces warm ammoniacal silver solutions. When treated with concentrated hydrobromic acid at 0°, it yields a crystalline compound of the composition $C_7H_{12}OBr_2$; this substance melts at 34·5°, and is very readily soluble in alcohol, chloroform, carbon bisulphide, ether, and benzene, but insoluble in cold water; it is decomposed by boiling water and by alkalis, being reconverted into the oxetone.

γ-Ethoxybutyric acid, $OEt\cdot[CH_2]_3\cdot COOH$, is obtained as a brown

oil when the alkaline solution referred to above is acidified and then extracted with ether; it is a thick liquid boiling at 231°. The *calcium* salt $(C_6H_{11}O_3)_2Ca + 2H_2O$, separates from water in rosette-shaped crystals, loses its water at 115°, and melts at 140°; it is readily soluble in alcohol. The *silver* salt, $C_6H_{11}O_3Ag$, is a colourless, amorphous compound, readily soluble in boiling water, and very stable in the light. When γ-ethoxybutyric acid is heated with concentrated hydrochloric acid at 140°, it is converted into γ-chlorobutyric acid; this compound is decomposed by boiling water, yielding butyrolactone, from which γ-hydroxybutyric acid is easily obtained as a thick oil, boiling at 231°, and miscible with water in all proportions. F. S. K.

Divalolactone. By R. Fittig and W. D. Hoeffken (*Annalen*, **267**, 203—204).—Divalolactone (compare Fittig and Rasch, Abstr., 1890, 867), when purified by distillation, solidifies in a freezing mixture, and, after having been pressed between blotting paper, can be recrystallised from warm light petroleum, from which it is deposited in slender needles melting at 39°; it boils at 309° with slight decomposition. F. S. K.

Condensation of Pyruvic Acid with Dicarboxylic Acids. By R. Fittig and G. Parker (*Annalen*, **267**, 204—218).—Pyrocinchonic anhydride can be very easily and cheaply prepared by gradually heating a mixture of anhydrous sodium succinate, pyruvic acid, and acetic anhydride, in molecular proportion, to 110°, and then keeping the mixture at that temperature until the evolution of carbonic anhydride ceases, which is usually the case in from 20—30 hours; after cooling, the mixture is treated with warm water, and steam-distilled as long as the distillate shows an acid reaction. The distillate is mixed with excess of sodium carbonate, concentrated, acidified with hydrochloric acid, the crystalline precipitate extracted by shaking with ether, and finally recrystallised from hot water; the anhydride is obtained in this way in large, transparent plates melting at 95°.

Barium pyrocinchonate, $C_6H_6O_4Ba$, is deposited in small, nacreous, anhydrous plates when its solution in cold water is warmed; the *calcium* salt, $C_6H_6O_4Ca$, is also more readily soluble in cold than in hot water, and crystallises in lustrous, anhydrous plates. The *silver* salt, $C_6H_6O_4Ag_2$, is sparingly soluble in water. When the mixture of sodium succinate, pyruvic acid, and acetic anhydride referred to above is carefully heated at a temperature below 80°, the principal product is an acid which could not be obtained in a pure condition, but which is, in all probability, identical with the valerolactonedicarboxylic acid described by Rasch (*Annalen*, **234**, 35).

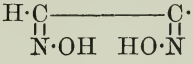
Uvic acid (pyrotritartaric acid), $C_7H_8O_3$, is obtained when a mixture of anhydrous sodium succinate and pyruvic acid is heated at 110° for about 36 hours; the product is isolated by distillation with steam.

Ethylmethylmaleïc acid, $C_7H_{10}O_4$, is formed by the mutual action of sodium glutarate, pyruvic acid, and acetic anhydride, in molecular

proportion, under the conditions described in the preparation of pyrocinchonic anhydride; the product is distilled with steam, and isolated by means of its crystalline *barium* salt, $C_7H_8O_4Ba$. The *calcium* salt, $C_7H_8O_4Ca + H_2O$, like the barium salt, is much more readily soluble in cold than in warm water, and is deposited in colourless plates when a cold, saturated solution is warmed. The *silver* salt, $C_7H_8O_4Ag_2$, crystallises from hot water in plates. When the barium salt is treated with hydrochloric acid, ethylmethylmaleïc anhydride is precipitated as an oil, which is moderately easily soluble in hot water, and miscible with alcohol, ether, &c., in all proportions (compare Bischoff, Abstr., 1891, 291); the yield is comparatively small. The solution of the original product, from which ethylmethylmaleïc acid has been separated, contains a syrupy acid which is in all probability dimethylbutyrolactonedicarboxylic acid; when this substance is distilled, it is converted into ethylmethylmaleïc anhydride (b. p. 232—233°) with evolution of carbonic anhydride; the quantity of anhydride obtained in this way is much larger than that prepared directly from the crude product in the manner described above. F. S. K.

Action of Hydroxylamine on Dibromopyruvic Acid. By H. G. Söderbaum (*Ber.*, **25**, 904—916).—*Primary dihydroximidopropionic acid*, $C_3H_4N_2O_4$, is obtained by cautiously mixing aqueous solutions of dibromopyruvic acid (60 grams), hydroxylamine hydrochloride (48 grams), and anhydrous sodium carbonate (80—90 grams), at a low temperature; after remaining at 10—15° for 1—2 days, the precipitated crystals are collected, dissolved in dilute sulphuric acid, and the solution extracted with ether. The pure compound crystallises in tufts of small, white needles containing 1 mol. H_2O, sinters at 80° with the loss of water, melts at 141—143°, and is readily soluble in water, alcohol, and ether, but almost insoluble in benzene. Its aqueous solution has an acid reaction, gives a blood-red colour with ferric chloride, a dark-violet with ferrous sulphate and sodium hydroxide, and an amorphous, olive-green precipitate with copper acetate. The *sodium* salt, $C_3H_3N_2O_4Na + 3H_2O$, crystallises in large, four-sided tables; the *silver* salt, the *ammonium* salt, the *calcium* salt, with $2H_2O$, and the barium salt, with $5H_2O$, were also prepared. The *diacetyl* derivative, obtained by treating the anhydrous acid at the ordinary temperature, or at 90—100°, with acetic anhydride, and allowing the solution to evaporate in a vacuum over potash, forms six-sided tables, and melts at 135° with the evolution of gas; it also crystallises from a small quantity of water in monhydrated, four-sided tables melting at 90—92° with the evolution of gas; it dissolves in ether, alcohol, and chloroform, but is insoluble in benzene, and when treated with a large quantity of water, or with alkali, it is hydrolysed with the formation of secondary dihydroximidopropionic acid (see below). When the diacetyl derivative is heated at 130—140°, it is decomposed into carbonic anhydride, acetic acid, and acetylhydroximidoacetonitrile melting at 46° (see below). When primary dihydroximidopropionic acid is dissolved in water, and hydrogen chloride is passed through the solution, it decomposes into the secondary acid, cyanogen, carbonic anhydride, and water; whilst if the acid is boiled in a

reflux apparatus with concentrated aqueous alkali, a salt of isonitrosomalonic acid is obtained.

Secondary dihydroximidopropionic acid is prepared by heating the mother liquor from the primary acid at 50—60°, or by treating the primary acid with hydrogen chloride, as above described; the anhydrous acid forms a white, crystalline powder, and melts at 172° with decomposition, but it crystallises from dilute sulphuric acid in long, delicate needles containing water of crystallisation, and melting at 156°; it resembles the primary acid in its reactions. The *sodium salt*, with $2H_2O$, crystallises in white needles, the *ammonium salt*, the *silver salt*, with $2H_2O$, the *calcium salt*, with $4H_2O$, and the *barium salt*, with $2H_2O$, are also described. When treated with acetic anhydride at temperatures ranging between 15° and 100°, *acetylhydroximidoacetonitrile*, CN·CH:NOAc, which crystallises in jagged needles, and melts at 46°, is obtained. The *acetyl derivative* is obtained in small quantity by digesting the acid for several days with acetic chloride, and is separated from unattacked acid by means of ether; it crystallises with 1 mol. H_2O in colourless needles or prisms, and melts at 90°; whilst, after remaining in the desiccator, it is dehydrated, and then melts at 133°; the secondary acid is obtained by hydrolysing it, and it gives isonitromalonic acid when boiled with concentrated alkali. Taking the above described facts into account, the author assigns the configuration  (*carboxysynglyoxime*) to the primary acid, and the configuration  (*syncarboxyamphiglyoxime*) to the secondary acid. A. R. L.

Constitution of Ethyl Acetoacetate and of the so-called Ethyl Formylacetate. By H. v. Pechmann (*Ber.*, **25**, 1040—1054; compare this vol., p. 696).—When ethyl acetoacetate is shaken with soda and benzoic chloride, it yields a mono- and a di-benzoyl derivative, whereas Wislicenus' "ethyl formylacetate" gives only a monobenzoyl derivative. The monobenzoyl derivative of ethyl acetoacetate has still the properties of ethyl acetoacetate, in so far as it has an acid character, which it loses, however, on the introduction of a second benzoyl group; "ethyl formylacetate," on the other hand, loses its acid character on the introduction of a single benzoyl group. It follows, therefore, that ethyl acetoacetate contains two, "ethyl formylacetate" only one hydrogen atom replaceable by acid radicles; in the former, the benzoyl group combines directly with carbon, but the latter gives a benzoate, as will be shown below, the benzoyl group replacing the hydrogen atom of a hydroxyl radicle.

These facts, and other experiments described below, prove that ethyl acetoacetate and "ethyl formylacetate" are quite differently constituted; the latter contains a hydroxy-group, and is ethyl β-hydroxyacrylate, OH·CH:CH·COOEt, whereas ethyl acetoacetate, both in the free condition and in its metallic derivatives, has the ketone constitution, otherwise it must behave like ethyl hydroxyacrylate (compare Brühl, this vol., p. 583). Although this conclusion

is directly opposed to that arrived at by Nef (this vol., p. 147), the author agrees with Nef that it is unnecessary to assume that ethyl acetoacetate exists in tautomeric forms, not, however, because the existence of tautomeric forms should be denied in all cases, but for the simple reason that all the reactions of ethyl acetoacetate can be explained on the basis of the ketone formula.

The author then describes the preparation and the manner of separating the two acetyl and the two benzoyl derivatives of ethyl acetoacetate; the syrupy dibenzoyl derivative and the diacetyl derivative (ethyl triacetylacetate) were found to be identical with the compounds described by Nef (*loc. cit.*); the monobenzoyl derivative boils at 202° under a pressure of 50 mm., and its copper derivative melts at 224°, not at 180—190°, as stated by James (*Annalen*, **226**, 220). When an alkaline solution of ethyl acetoacetate is treated with ethyl chloroformate, a large quantity of a neutral substance, probably the dicarboxethyl derivative, and a trace of a substance which is soluble in soda, and which is probably ethyl acetylmalonate, are formed. Ethyl β-hydroxyacrylate ("ethyl formylacetate"), prepared by the method described by Wislicenus (Abstr., 1888, 129), gives, with copper acetate and a few drops of ammonia, a crystalline copper derivative, which separates from dilute alcohol in yellowish-green needles, and from benzene in plates, melting at 168°. The *benzoyl* derivative, OBz·CH:CH·COOEt, prepared by shaking a cold alkaline solution of the sodium derivative with benzoic chloride, melts at 5°, boils at 208—209°, under a pressure of 50 mm., and is insoluble in alkalis; its alcoholic solution gives no coloration with ferric chloride and no precipitate with copper acetate; when the benzoyl derivative is treated with bromine in well-cooled chloroform solution, it yields a colourless, oily dibromo-additive product, which decomposes on keeping, seemingly into benzoic bromide and ethyl hydroxybromacrylate. The *acetyl* derivative, OAc·CH:CH·COOEt, prepared in like manner, or better, by gradually adding acetic chloride to ether containing the sodium derivative of ethyl β-hydroxyacrylate in suspension, is a colourless liquid boiling at 126° under a pressure of 46 mm.; it is insoluble in water and alkalis, and gives no reaction with ferric chloride or with copper acetate, but it is very readily hydrolysed even by cold sodium carbonate.

Ethyl β-acetoxy-αβ-dibromopropionate,

OAc·CHBr·CHBr·COOEt,

is formed when the acetyl derivative of ethyl hydroxyacrylate is treated with bromine in well-cooled chloroform solution; it is a thick, colourless oil, boils at 154° with slight decomposition under a pressure of 34 mm., and decomposes on keeping.

Ethyl β-acetoxymethylacrylate, OAc·CH:CMe·COOEt, prepared by heating ethyl β-hydroxymethylacrylate ("ethyl formylpropionate") with acetic anhydride at 140°, is a colourless liquid boiling at 132° under a pressure of 48 mm.; it is insoluble in alkalis, and gives no reaction with ferric chloride. The corresponding *benzoyl* derivative, OBz·CH:CMe·COOEt, crystallises from dilute alcohol in long, lustrous needles, melts at 55°, and dissolves freely in all ordinary solvents.

except water and light petroleum; it is insoluble in soda, and gives no colour reaction with ferric chloride.

Ethyl β-anilidoacrylate, NHPh·CH:CH·COOEt, is precipitated when an aqueous solution of the sodium derivative of ethyl hydroxyacrylate is gradually added to a solution of aniline in dilute acetic acid; it separates from alcohol in almost colourless plates, melts at 106°, and is insoluble in water and light petroleum, but very readily soluble in other ordinary solvents. It is insoluble in soda, but it dissolves in concentrated hydrochloric acid, yielding a solution from which water precipitates a colourless, flocculent substance, which is soluble in alkalis; its alcoholic solution gives a reddish-yellow coloration with ferric chloride. When dissolved in alcoholic potash, and precipitated with water, it is converted into a crystalline compound melting at 136°. Although this ethereal salt has, doubtless, the constitution assigned to it above, it is not identical with the ethyl β-anilidoacrylate prepared by Reissert (Abstr., 1888, 276) from the product of the action of aniline on dibromosuccinic acid.

Ethyl β-paratoluidoacrylate, C_6H_4Me·NH·CH:CH·COOEt, prepared in like manner, crystallises in yellowish plates, melts at 116°, and resembles the preceding compound in its behaviour with solvents; when treated with alcoholic potash, it is converted into a crystalline compound melting at 144°, and when warmed with acetic anhydride, it yields acetotoluidide.

Ethyl β-paratoluidodiacrylate, C_6H_4Me·N(CH:CH·COOEt)$_2$, can be prepared by heating an ethereal solution of ethyl hydroxyacrylate with ethyl toluidoacrylate, or by treating paratoluidine with ethyl hydroxyacrylate, ethyl β-chloracrylate, or ethyl β-benzoylhydroxyacrylate under the same conditions; it crystallises from alcohol in well-defined, lemon-yellow, transparent prisms, from dilute alcohol in lustrous, yellow needles, and melts at 73°.

When ethyl α-phenyl-β-hydroxyacrylate (ethyl formylphenylacetate) is oxidised with potassium permanganate in alkaline solution, it yields benzoylformic acid; ethyl β-hydroxyacrylate gives glyoxylic acid. F. S. K.

Ethyl Bromacetoacetates and Cyanacetoacetates. By A. Haller and A. Held (*Compt. rend.*, **114**, 452—455).—The authors have observed that ethyl bromacetoacetate, prepared according to Schönbrodt's method (Abstr., 1890, 27) is invariably accompanied by a small proportion of an isomeric liquid, which gives off hydrogen bromide and partially decomposes when boiled, and, like the similar compound prepared by Duisberg, yields ethyl succinosuccinate when treated with potassium cyanide.

In order to ascertain the structure of the isomeride, some bromacetoacetate, prepared and purified according to Schönbrodt's directions, was treated with dry potassium cyanide in ethereal solution, with the result that only 5 per cent. of the potassium and ethyl salts of the α-cyano-derivative, but 40 per cent. of the ethyl salt of the γ-cyano-derivative, was obtained. The identity of the latter was proved by treating it with a methyl alcohol solution of hydrogen chloride, when, in addition to the hydrochloride of the imido-com-

pound already described (Abstr., 1891, 171), an acetonedicarboxylic acid was obtained which, on further treatment with hydrocyanic acid and hydrochloric acid, was converted into citric acid. *Ethyl γ-cyanacetoacetate*, $CN\cdot CH_2\cdot CO\cdot CH_2\cdot COOEt$, is a colourless liquid, which boils at 135—140° under a pressure of 40 mm., and is insoluble in aqueous sodium carbonate.

That Schönbrodt's bromacetoacetate was really a mixture was further shown by treating it with thiocarbamide after Hantzsch's method, by which means the condensation products, ethyl μ-amidomethylthiazolcarboxylate and μ-amidothiazylacetate were obtained, which were described by that author as resulting from ethyl γ- and α-bromacetoacetates. The relative quantities of the products, however, seemed to show that the α-bromo-derivative was present in the greater proportion. Jn. W.

So-called Ethyl Carbacetoacetate. By A. Hantzsch (*Ber.*, **25**, 1310).—Genvresse (*Ann. Chim. Phys.* [6], **24**, 46) regards the chlorination product of ethyl acetoacetate as a γ-derivative; whereas Hantzsch and Schiffer (this vol., p. 697) have pronounced it to be an α-derivative. Genvresse further describes a large number of derivatives of the so-called ethyl carbacetoacetate, and proposes a constitutional formula for this substance; the author points out that the latter has already been shown by Polonoffska (Abstr., 1886, 1011) to be impure ethyl isodehydracetate. A. R. L.

Turkey-red Oil. By P. Juillard (*Bull. Soc. Chim.* [3], **6**, 638—656).—By methods similar to those described by Scheurer-Kestner (Abstr., 1891, 542, 665), the author has isolated several derivatives of ricinoleïc acid which result from the action of strong sulphuric acid on it and on castor oil. He states that, although the composition of the oil varies greatly with the conditions of its formation, the main products of the reaction are ricinoleïc and ricinoleosulphonic acids and their polymerides, the higher terms of which are but slightly soluble in water, whilst the special solvent action of the oil is due to the presence of diricinoleïc and diricinoleosulphonic acids, and perhaps to the presence of an easily-decomposable diricinoleosulphonic anhydride. The washed product of the primary reaction, when kept for some weeks at 20—30°, undergoes almost complete conversion into polyricinoleïc acids, and both ricinoleïc acid and castor oil, when treated with hydrochloric acid, behave similarly, the action being hastened at a temperature of 100°. The author has prepared acetylricinic, butyroricinic, and oleoricinic acids, which are oily liquids soluble in alcohol. T. G. N.

Amido- and Anilido-derivatives of Succinic Acid. By C. Hell and R. Poliakoff (*Ber.*, **25**, 640—652).—The action of ammonia on ethyl mono- and di-bromosuccinate has been again studied, previous observers having obtained discordant results. When ethyl monobromosuccinate is treated with a considerable excess of

10 per cent. aqueous ammonia, no reaction occurs at 0°, but at the atmospheric temperature, flakes of fumaric diamide,

$$CONH_2\cdot CH{:}CH\cdot CONH_2,$$

are deposited, and resinous products are also formed. If alcoholic ammonia is used, the same reaction takes place, but much more slowly. Curiously enough, the same substance is obtained from the dibromosuccinate, together with large quantities of resinous products. If, however, the dibromosuccinate be heated with alcoholic ammonia at 60—70°, ethyl imidosuccinamate, $NH<\begin{matrix}CH\cdot CONH_2\\ |\\ CH\cdot COOEt\end{matrix}$, is formed, together with resinous products. The same substance is obtained, although in much smaller quantity, from the monobromosuccinate under similar circumstances. At higher temperatures, ranging from 80° to 150°, nothing but resinous products were, as a rule, obtained; once only, when the dibromosuccinate was heated at 120—130° with alcoholic ammonia, was a crystalline product, *imidosuccinic diamide*,

$$NH<\begin{matrix}CH\cdot CONH_2\\ |\\ CH\cdot CONH_2\end{matrix}$$

obtained. This forms yellowish plates melting at 175—176°, dissolves in hot water, alcohol, ether, and acids, and is decomposed by alkalis, even in the cold, with liberation of ammonia.

If ethyl monobromosuccinate (1 mol.) is heated for 4 hours at 140—160° with aniline (4—5 mols.), some ethyl anilidosuccinate, $COOEt\cdot CH(NHPh)\cdot CH_2\cdot COOEt$, is formed, together with some *ethyl anilidophenylsuccinamate*, $NHPh\cdot CO\cdot CH(NHPh)\cdot CH_2\cdot COOEt$, and much anilidosuccinic dianilide,

$$NHPh\cdot CO\cdot CH(NHPh)\cdot CH_2\cdot CONHPh.$$

The second substance may be obtained by extracting the product of the reaction successively with cold ether and acetic acid, and crystallising the residue from hot absolute alcohol. It forms fine, yellow prisms, melts at 144°, turning brown and evolving gas, dissolves but sparingly or is insoluble in the usual solvents, and is decomposed by alkalis, with formation of aniline and the anilido-acid. If, instead of 4—5, only about 3 mols. of aniline are used in the reaction, and the temperature is kept somewhat lower, anilidosuccinanil, $\begin{matrix}CH(NHPh)\cdot CO\\ |\\ CH_2\text{———}CO\end{matrix}>NPh$, is also formed, and in greater quantity, as the reaction lasts longer. C. F. B.

Fermentation. By E. Buchner (*Ber.*, **25**, 1161—1163).—Hydrogen ammonium fumarate and ammonium fumarate are acted on by *Penicillium glaucum* at ordinary temperatures, and by *Aspergillus niger* at 30—35°, whilst the corresponding maleïc salts are unaffected by these organisms. For experimental details, the original paper should be consulted. J. B. T.

Action of Heat on the Hydrogen Malates of Methylamine and Benzylamine. By E. Giustiniani (*Gazzetta*, **22**, i, 169—176).

—On heating ethylamine hydrogen malate, Piutti (Abstr., 1889, 590) obtained ethylfumarimide and an amorphous condensation product which could not be converted into inactive aspartic acid.

The author finds that, on heating methylamine hydrogen malate at 200°, it gives a large quantity of an amorphous condensation product which does not yield methylaspartic acid when heated with hydrochloric acid in a sealed tube at 150°. A small quantity of *methylfumarimide*, $\begin{matrix}CH\cdot CO\\ \|\\ CH\cdot CO\end{matrix}>NMe$, is also formed and distils over. It crystallises in long, white prisms, melts at 90—92°, and is soluble in alcohol, less so in water and ether, and only very sparingly in benzene. It readily volatilises, and provokes tears. It yields a bromo-compound melting at 97°, and, when fused with caustic potash, gives off methylamine, leaving potassium fumarate in the residue. It dissolves in cold caustic potash, forming a reddish solution which deposits *methylfumaramic acid*, NHMe·CO·CH:CH·COOH, when hydrochloric acid is added. This substance forms small, white crystals melting at 149°, and combines with bromine in the cold. It is soluble in water and alcohol, sparingly so in ether. The *silver* salt is a white, amorphous powder not altered by light.

On heating benzylamine hydrogen malate at 200°, benzylfumarimide and two isomeric benzylmalimides are obtained, together with an amorphous condensation product which is not altered by heating with hydrochloric acid at 200° in a sealed tube. *Benzylfumarimide*, $\begin{matrix}CH\cdot CO\\ \|\\ CH\cdot CO\end{matrix}>N\cdot CH_2Ph$, separates from its alcoholic solution in splendid prisms melting at 67·5°. It is very soluble in hot alcohol and ether, sparingly so in water; it has a pungent taste, and its boiling ethereal solution takes up bromine, giving a liquid bromo-compound. On dissolving it in a mixture of sulphuric and nitric acids, a nitro-derivative is obtained which crystallises from alcohol in yellow needles, and melts at 173°. It dissolves in cold caustic potash forming *benzylfumaramic acid*, $CH_2Ph\cdot NH\cdot CO\cdot CH{:}CH\cdot COOH$, which separates, on adding hydrochloric acid, in small, white crystals melting at 183°. It is soluble in water, alcohol, and ether, but only very sparingly in benzene. It yields a white, amorphous *silver salt* which is rapidly changed by light, and explodes on heating. Both benzylfumarimide and benzylfumaramic acid give benzylamine on fusion with caustic potash. When the residue obtained on heating benzylamine hydrogen malate is extracted with hot water, two isomerides are dissolved. The less soluble one crystallises in square tablets melting at 114°, and is *α-benzylmalimide*, $C_{11}H_{11}NO_3$; it is soluble in acetic acid, hot water, alcohol, and ether, less so in benzene. The more soluble compound is *β-benzylmalimide;* it crystallises in acicular prisms, melts at 105°, and is soluble in acetic acid, alcohol, and ether, very sparingly so in benzene. On heating at 200—210° it is partly polymerised and partly decomposed into water and benzylfumarimide; the α-modification, when similarly treated, merely sublimes unchanged. Both α- and β-imides dissolve in caustic potash (20 per cent.) with formation of benzylmalamic acid. On treating them with

hot concentrated potash, benzylamine and potassium malate are produced. They both dissolve unaltered in acetic anhydride. On treatment with acetic chloride, the α-compound yields an *acetyl* derivative which melts at 90°, and is very sparingly soluble in water; the β-imide gives an *acetyl* derivative which melts at 102°, and is very soluble in alcohol and ether. The *benzoyl* derivative of α-benzylmalimide crystallises in small needles and melts at about 100°. The *benzoyl* derivative of the β-imide crystallises in needles melting at 122°.

Benzylmalamic acid, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, obtained by dissolving the benzylmalimides in cold aqueous potash (20 per cent.), and treating the solution with hydrochloric acid, forms small, white crystals melting at 130—132°. It is very soluble in alcohol, ether, and boiling water, sparingly so in cold water. Its *silver* salt is a white, crystalline powder, slowly altered by light. The *monacetyl* derivative forms a whitish, crystalline powder, soluble in alcohol and ether, sparingly so in water, and melts at 87°. The *benzoyl* derivative is obtained as very minute, white crystals melting at 117°. It is very soluble in alcohol and ether, sparingly so in water, and on boiling with water gives benzoic acid. W. J. P.

Synthesis of Tartaric Acid. By P. Genvresse (*Compt. rend.*, **114**, 555—557).—Glyoxylic acid was treated with zinc powder in presence of acetic acid diluted with its own weight of water, first at the ordinary temperature, and afterwards on the water-bath. The zinc is added gradually to the mixture of the two acids, the proportions of the molecules being, glyoxylic acid, 1; acetic acid, 3; zinc 2. Under these conditions glyoxylic acid is converted into tartaric (racemic) acid, the reaction being analogous to the conversion of acetone into pinacone, or benzaldehyde into hydrobenzoïn. The racemic acid was identified by the behaviour of the calcium salt, the reduction of ammoniacal silver nitrate, and the isolation of the free acid and measurement and analysis of the crystals. C. H. B.

Optically Isomeric Gulonic Acids. By E. Fischer and R. S. Curtiss (*Ber.*, **25**, 1025—1031).—The compound (m. p. 160°) previously described as *i*-gulonolactone (Abstr., 1891, 668) is simply a mechanical mixture of the *d*- and *l*-lactones; when a solution of equal quantities of the two optically active lactones is allowed to evaporate slowly, such large crystals of the two compounds are formed that they can be separated mechanically. The fact that the racemic modification of gulolactone cannot be obtained by crystallisation from water is of general interest, but not without analogy. A further examination of the two active lactones has shown that they are crystallographical antipodes.

i-Gulonic acid is obtained in the form of its *calcium* salt,

$$(C_6H_{11}O_7)_2Ca,$$

when an aqueous solution of equal quantities of the two optically active lactones is boiled with calcium carbonate. This salt crystallises from hot water in very slender needles, and contains water

of crystallisation, which is slowly given up on keeping over sulphuric acid; 100 parts of water at 15° dissolve only 1·6 parts of the anhydrous salt, whereas the same quantity of water at the same temperature dissolves 5·8 grams of the anhydrous calcium salt of *l*-gulonic acid. A solution of the acid, prepared by heating a solution of the calcium salt with 10 per cent. hydrochloric acid, is optically inactive.

i-Gulonic acid phenylhydrazide, $C_6H_{11}O_6{\cdot}N_2H_2Ph$, is deposited in yellow crystals when a concentrated, optically inactive solution of the two lactones is heated at 100° with phenylhydrazine for an hour, and then allowed to cool. It crystallises from hot alcohol in slender needles, melts and slowly decomposes at 153—155°, and is very readily soluble in hot, but only moderately easily in cold, water. A 10 per cent. aqueous solution of the hydrazide is optically inactive, whereas a 9 per cent. solution of the corresponding derivative of *l*-gulonic acid is feebly dextrorotatory; as the two compounds differ also in melting point, and in the readiness with which they crystallise from alcohol, it is very probable that the inactive hydrazide just described is really the racemic modification, and not simply a mechanical mixture.

i-Gulose can be obtained as a colourless syrup by reducing a mixture of the two lactones with sodium amalgam in the usual manner. The *phenylhydrazone*, $C_6H_{12}O_5{:}N_2HPh$, crystallises from alcohol in slender, colourless needles, melts at 143°, and is sparingly soluble in cold water; a 7 per cent. aqueous solution of this compound, examined at 50° in a tube 1 dm. in length, was found to be optically inactive, but in other respects the hydrazone resembles the corresponding derivative of *l*-gulose so closely that it is impossible to say with certainty whether it is the racemic modification or a mechanical mixture.

i-Phenylgulosazone, $C_6H_{10}O_4(N_2HPh)_2$, crystallises from warm ethyl acetate in slender, yellow needles, melts at 157—159°, and is much more sparingly soluble in hot water than *l*-phenylgulosazone, from which it also differs in its manner of crystallising; as, moreover, the new compound is optically inactive, it is doubtless the racemic modification.

i-Phenylgulosazone resembles phenyl-*β*-acrosazone so closely in melting point, crystalline form, solubility in water, and in optical behaviour, that the two compounds might be considered to be identical, were it not that the former requires for solution about four times as much ethyl acetate as the latter. That the two compounds are not identical was also proved by a comparison of their bromo-derivatives. *Parabromophenylgulosazone*, prepared by heating gulose with a dilute alcoholic solution of bromophenylhydrazine acetate at 100°, crystallises from ethyl acetate in slender, yellow needles, melts at 180—183° when quickly heated, and decomposes at a slightly higher temperature. The corresponding derivative of *β*-acrose, obtained by warming a dilute aqueous solution of *β*-acrosone with bromophenylhydrazine and acetic acid, melts at 180—183°, and is much more readily soluble in ethyl acetate than the isomeride just described. The conjecture that *β*-acrosazone might be inactive gulosazone consequently falls to the ground. F. S. K.

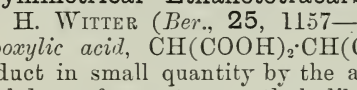
Citric Acid. By E. Buchner and H. Witter (*Ber.*, **25**, 1159—1160).—H. Kämmerer's "isomalic acid" appears to be anhydrous citric acid; it is readily prepared by heating citric acid in aqueous solution until the temperature rises to 130°; on cooling, the anhydrous acid is deposited in colourless crystals which melt at 153°, and are unacted on by water. On adding a crystal of the hydrated acid to a concentrated aqueous solution of the anhydrous acid at the ordinary temperature, the hydrated acid separates in crystals, but the converse does not apply. Both acids yield identical methyl salts, but the lead salts are not identical; for, on treatment of these compounds with hydrogen sulphide, the original anhydrous or hydrated acid is regenerated.

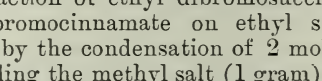
Hydrated citric acid melts between 135° and 152°, not at 100° as stated in text-books. J. B. T.

Symmetrical Ethanetetracarboxylic Acid. By E. Buchner and H. Witter (*Ber.*, **25**, 1157—1158).—Symmetrical *ethanetetracarboxylic acid*, $CH(COOH)_2 \cdot CH(COOH)_2$, is obtained as a bye-product in small quantity by the action of ethyl dibromosuccinate, ethyl bromofumarate, or ethyl dibromocinnamate on ethyl sodiomalonate, and is therefore formed by the condensation of 2 mols. of malonic acid. It is prepared by boiling the methyl salt (1 gram) with soda (4·5 c.c.) of sp. gr. 1·2, and water (4·5 c.c.), for 1·5 hours, and crystallises from ether in small needles which melt at 167—169° with evolution of gas; on heating for some time at 180°, succinic acid is formed.

The *methyl salt* is deposited from ether, in which it is sparingly soluble, in small, colourless crystals melting at 138°. J. B. T.

Reduction of Mucic Acid. By E. Fischer and J. Hertz (*Ber.*, **25**, 1247—1261).—According to theory, two optically inactive bibasic acids are capable of existence, having the configurations:—





Van't Hoff (*Die Lagerung der Atome in Raume*, S. 39) regarded mucic acid as one of them, and the so-called paramucic acid, which has been shown to be mucic acid lactone (Abstr., 1891, 1193), as the other. Later, Van't Hoff altered his views (*Dix années dans l'histoire d'une théorie*, p. 60) in accordance with Bouchardat's observation that dulcitol yields optically active derivatives; and, therefore, in spite of their apparent inactivity, both dulcitol and mucic acid must be represented as optically active systems. Dulcitol and mucic acid have also been regarded as "racemic" compounds by Carlet (*Jahresber.*, 1860, 250). If mucic acid is an optically inactive com-

pound in virtue of the spacial symmetry of its molecule, it might be expected that on reduction both carboxyl groups would be equally attacked, and that the resulting inactive monobasic acid would be separable into two oppositely active components, both of which would yield mucic acid on oxidation. The experiments described below show this to be the case.

Reduction of Mucic Acid Lactone.—Commercial mucic acid, which contains unknown optically active impurities, is purified by dissolving it in the smallest possible quantity of hot dilute sodium hydroxide solution, treating with animal charcoal, and adding hydrochloric acid to the filtrate, when the pure acid separates and is washed with cold water; that portion which is converted into the lactone is reconverted into the acid by evaporating the filtrate with an excess of hydrochloric acid, and recovered. The purified acid (150 grams) is boiled with water (60 parts) until it dissolves, and the solution is evaporated to $1\frac{1}{2}$ litres; the mucic acid which separates on cooling is removed, and the filtrate containing the lactone is cooled to 0°, and treated with $2\frac{1}{2}$ per cent. sodium amalgam with frequent shaking. At a certain stage in the reduction it is necessary to keep the solution acid by the frequent addition of dilute sulphuric acid, but after its cupric reducing power has attained its maximum, that is, when all the lactone is converted into aldehyde acid, it is kept faintly alkaline during the addition of the remaining portion of the amalgam. The operation, which usually lasts about seven hours, is stopped when 12 parts of the solution do not completely reduce 1 part of Fehling's solution; 2—$2\frac{1}{2}$ kilos. of amalgam are generally required. The solution is decanted from mercury and the filtrate evaporated to the crystallising point of sodium sulphate; concentrated sulphuric acid (50 grams) and hot 96 per cent. alcohol are then added. After cooling, the filtrate is evaporated with addition of water until the alcohol is removed; when the aqueous liquid is boiled with barium carbonate for half an hour, a barium salt, amounting to 45 per cent. of the lactone employed, is obtained in delicate, white needles on evaporating the filtrate. Details are also given of the reduction of diethyl mucate by sodium amalgam, but by this method i.-galactonic acid hydrazide corresponding only with 2 per cent. of the ethyl salt is obtained. *i.-Galactonic acid*, $C_6H_{12}O_7$:—The last-mentioned barium salt is dissolved in water, exactly precipitated by sulphuric acid, and the filtrate evaporated, when an optically inactive mixture of the acid and lactone separates. To obtain the *lactone*, $C_6H_{10}O_6$, the last product is dissolved in about $\frac{1}{3}$ its weight of warm water, and the crystals which separate after some days are collected, washed with alcohol, and later with acetone, and finally crystallised from boiling acetone. It is thus obtained in delicate prisms; it melts at 122—125°, exhibits no appreciable optical rotation in 10 per cent. aqueous solution, dissolves readily in water, somewhat sparingly in alcohol and pure acetone, and very sparingly in ethyl acetate, and is easily converted into mucic acid by nitric acid. The *barium* and *calcium* salts both crystallise with $2\frac{1}{2}$ mols. H_2O, the latter being very sparingly soluble in boiling water; the *cadmium* salt crystallises with 1 mol H_2O; whilst the *phenylhydrazide*, $C_{12}H_{18}N_2O_6$, obtained by heating a 20 per cent.

aqueous solution of the lactone with an equal quantity of phenylhydrazine on the water-bath for an hour, crystallises from water or dilute alcohol in stellate groups of colourless needles, and melts at about 205° with decomposition. *i.-Galactose*, $C_6H_{12}O_6$, is prepared by reducing a 10 per cent. cold aqueous solution of the lactone in the usual manner with nine times its weight of sodium amalgam. The solution decanted from mercury is rendered alkaline and boiled, exactly neutralised with sulphuric acid, and sufficient absolute alcohol added until it contains 85 per cent. of the latter. The sodium salt which separates is again treated with alcohol in the same way until it is free from the sugar, and the united alcoholic solutions are evaporated to a syrup, when crystallisation commences after some days. It is then triturated with methyl alcohol, and the collected crystals washed with the same liquid, dissolved in boiling absolute alcohol, filtered from insoluble matter, evaporated in a vacuum, and the syrup placed over concentrated sulphuric acid; the sugar which separates is then washed with alcohol and ether. It melts not quite constantly between 140° and 142°, and is optically inactive; it does not exhibit a characteristic crystalline form, but the question whether it is a "racemic" compound or a mechanical mixture of the two isomerides is not decided. Its derivatives are optically inactive. The *phenylhydrazone* forms colourless leaflets, and melts at 158—160°; the phenylosazone melts at 195°, and is undoubtedly identical with that obtained from dulcitol (Abstr., 1888, 358).

i.-Galactonic acid may be separated into its optically active components by the method employed for the separation of i.-mannonic acid (Abstr., 1890, 467). The lactone (20 grams) is dissolved in 70 per cent. alcohol (600 c.c.), and the solution boiled for an hour with finely pulverised strychnine (50 grams); the filtrate is evaporated with the addition of water until all the alcohol is removed, when the excess of strychnine separates, and after evaporating this filtrate to a thin syrup, white needles consisting chiefly of the d.-salt separate; it is recrystallised from alcohol, converted into the barium salt, and thence into the calcium salt. The latter is boiled with twice its weight of water, when only the d.-salt passes into solution, and separates from the filtrate in the pure state on cooling; it has all the properties of calcium d.-galactonate, and gives the lævorotatory lactone described by Tollens and others (Abstr., 1891, 43). l.-Galactonic acid is obtained by boiling the mother liquor from strychnine d.-galactonate with barium hydroxide, exactly precipitating the solution of the barium salt with sulphuric acid, boiling the filtrate with calcium carbonate, and evaporating this filtrate to a syrup, when a mixture of the l.- and i.-calcium salts separates. It is boiled with twice its weight of water, when the l.-salt dissolves, and separates from the filtrate in five-sided plates, closely resembling the d.-salt. When it is heated at 100°, it loses 15 per cent. of its weight, and when 0·2 gram is heated at 100° in a sealed tube with 0·91 per cent. hydrochloric acid (4 c.c.), the solution shows an optical activity of 2·71° in a 100-mm. tube, due to the formation of a dextrorotatory lactone.

l.-Galactose, $C_6H_{12}O_6$, is obtained by the fermentation of i.-galactose; the crude syrup obtained by reducing i.-galactonic lactone is dissolved

in water (10 parts), fresh, washed, active beer yeast added, and the mixture placed in an incubator at 30°. Fermentation commences after two hours, and is generally complete at the end of 5—6 days. The filtered solution is boiled with animal charcoal, evaporated, and the crystals washed with methyl alcohol, again treated in dilute aqueous solution with animal charcoal, and evaporated; the syrup is then triturated with methyl alcohol, and the crystals boiled with absolute alcohol, the resulting solution evaporated to incipient turbidity, and the crystals obtained from the filtrate repeatedly recrystallised from alcohol. The compound melts at 162—163; whereas, according to v. Lippmann (*Ber.*, **18**, 3335), d.-galactose melts at 168°. The l.-galactose possessed a specific rotatory power in 10 per cent. aqueous solution eight minutes after preparation, $[\alpha]_D = -120$, and this ultimately became $[\alpha]_D = -73{\cdot}6$ to $-73{\cdot}7$ on remaining. The *phenylhydrazone* is dextrorotatory, and melts at 158—160°; the *phenylosazone* melts at 192—195°; l.-galactose yields mucic acid on oxidation with nitric acid and dulcitol on reduction with sodium amalgam. A. R. L.

So-called Artificial Pectic Acid from Fir-wood. (Oxycellulose.) By J. B. Lindsey and B. Tollens (*Annalen*, **267**, 366—370). The authors have made a number of analyses of the compound, obtained by the action of nitric acid on fir-wood, which Sacc considered to be pectic acid, but which, according to Porter, is a totally different substance. This product was found to contain 1·72—1·76 per cent. of ash, and the composition of the organic matter may be expressed by the formula $(C_6H_{10}O_5)_n$, or better still, by the formula $6C_6H_{10}O_5 + O$; the properties and reactions of the substance agree to some extent with those of the preparations described by Sacc and by Porter, and also with those of Cross and Bevan's oxycellulose (Trans., 1883, 22). When freed from nitric acid, it has a gelatinous character, and swells up when treated with water, so that it cannot be separated by filtration; when it is washed with a mixture of nitric acid and 60 per cent. alcohol, then repeatedly with 93 per cent. alcohol and ether successively, and dried over sulphuric acid, it is obtained in the form of a colourless powder, which dissolves completely in dilute ammonia, and in very dilute soda, being reprecipitated as a jelly on the addition of more concentrated soda or nitric acid. From a study of its properties, the authors conclude that it is not to be classed with the true pectin substances, as it does not contain pentoses, but that it is closely related to cellulose. F. S. K.

Bromacetamide. By E. Buchner and A. Papendieck (*Ber.*, **25**, 1160—1161).—Bromacetamide is prepared by treating ethyl bromacetate with two volumes of 10 per cent. aqueous ammonia at −10°; the product is deposited after some time, and crystallises from alcohol in colourless, flat needles which melt at 91°, not 165° as usually stated. J. B. T.

γ-Substituted Hydantoïns and Carbamido-acids. By I. Guareschi (*Chem. Centr.*, 1892, i, 140; from *Gior. R. Accad. Med.*,

1891).—The author has prepared γ-substituted hydantoïns and carbamido-acids by the action of mono-substituted carbamides on amido-acids. *γ-Methylhydantoïn*, $CO<\begin{matrix}NH—CH_2\\ NMe\cdot CO\end{matrix}$, is obtained from methylcarbamide and glycocine; *γ-phenylhydantoïn*, $CO<\begin{matrix}NH—CH_2\\ NPh\cdot CO\end{matrix}$ is obtained from phenylcarbamide and glycocine; *methylparaphenylglycoluric acid*, $NHMe\cdot CO\cdot NH\cdot C_6H_4\cdot COOH$, from methylcarbamide and paramidobenzoic acid; *phenylparaphenylglycoluric acid*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot COOH,$$

from phenylcarbamide and paramidobenzoic acid. J. W. L.

γ-Substituted Hydantoïns. By E. Quenda (*Chem. Centr.*, 1892, i, 140; from *Gior. R. Accad. Med.*, 1891).—From paratolylcarbamide and glycocine, the author has prepared *γ-paratolylhydantoïn*,

$$CO<\begin{matrix}NH——CH_2\\ N(C_6H_4Me)CO\end{matrix}.$$

Some ditolylcarbamide was formed at the same time. From the orthotolylcarbamide, the corresponding hydantoïn was obtained.

J. W. L.

Formation of Hydroxamic Acids of the Fatty Acids by means of Acid Anhydrides. By L. Crismer (*Ber.*, **25**, 1244; compare Miolati, this vol., p. 698).—A claim of priority. H. G. C.

Compounds of Thiophen and of its Homologues, and of some Ketones, with Mercuric Chloride. By J. Volhard (*Annalen*, **267**, 172—185).—When thiophen is shaken with a cold, saturated, aqueous solution of mercuric chloride, a voluminous, colourless precipitate is produced, and the solution acquires an acid reaction; a little alcohol is added in order to prevent the precipitate caking together, and the free hydrochloric acid produced in the reaction is got rid of by the addition of sodium acetate; the colourless precipitate is separated by filtration, washed with cold water, and then repeatedly extracted with boiling alcohol.

Thiophen mercuric chloride, $C_4SH_3\cdot HgCl$, separates from the alcoholic extract on cooling in colourless plates; it melts at 183°, sublimes at temperatures above 100°, and is almost insoluble in cold, and only moderately easily soluble in boiling, water; it is readily decomposed by hydrochloric acid, yielding thiophen and mercuric chloride. The portion of the precipitate which is insoluble in alcohol is a colourless powder of the composition $C_4SH_2{:}Hg_2Cl_2$; it is insoluble in all neutral solvents, is not acted on by alkalis, and is only slowly decomposed even by concentrated nitric acid.

When thiophen mercuric chloride, $C_4SH_3\cdot HgCl$, is boiled for some time with acetic chloride, it yields acetothienone, or thienyl methyl ketone, C_4SH_3Ac, identical with the compound previously described by Peter (Abstr., 1885, 141); the yield is 77 per cent. of the theoretical. When treated with benzoic chloride in like manner, it gives

phenyl thienyl ketone (m. p. 56°), identical with the compound prepared by Comey (Abstr., 1884, 1168). It is also readily acted on by iodine in presence of warm water, being converted into diiodothiophen (m. p. 40°).

α-Methylthiophen mercuric chloride, $C_5SH_5{\cdot}HgCl$, is formed, practically as sole product, when α-methylthiophen is shaken with an aqueous solution of mercuric chloride and sodium acetate; it crystallises from boiling alcohol in short, transparent needles, melts at 197°, and is insoluble in water and ether. When warmed with benzoic chloride for a long time, it yields phenyl thiotolyl ketone, a compound which has been previously described by Ernst (Abstr., 1887, 238) as an oil, but which the author obtained in lustrous needles melting at 124°.

β-Thiotolene mercuric chloride, $C_5SH_5{\cdot}HgCl$, prepared from thiotolene in like manner, crystallises from hot alcohol in slender, lustrous needles. The *dimercuric chloride*, $C_5SH_4{:}Hg_2Cl_2$, is a colourless, granular powder, insoluble in all neutral solvents, and only slowly acted on even by concentrated nitric acid.

β-Isopropylthiophen mercuric chloride, $C_7SH_9{\cdot}HgCl$, crystallises from hot alcohol in long, colourless needles, melts at 137°, and is soluble in ether, but insoluble in water; the *dimercuric chloride*, $C_7SH_8{:}Hg_2Cl_2$, is a colourless, granular compound, insoluble in all neutral solvents, and only slowly decomposed by concentrated nitric acid.

Acetothienone combines with mercuric chloride under the conditions already described yielding a compound of the composition $C_6H_6OS,HgCl_2$; this substance crystallises in long, colourless needles, melts at 68°, and is soluble in ether. Acetophenone, under the same conditions, gives a compound of the composition $C_8H_8O,HgCl_2$, which crystallises in large, colourless needles, melts at 59°, and is soluble in water, ether, and alcohol. The compound obtained with benzophenone crystallises in long, colourless needles, melts at 81°, and is readily soluble in water, alcohol, and ether; it has the composition $C_{13}H_{10}O,HgCl_2$. All these additive compounds are very readily decomposed, and on exposure to the air, the ketone contained in them gradually volatilises. F. S. K.

β-Ethylthiophen and Thiophen-αβ-dicarboxylic Acid. By M. Gerlach (*Annalen*, **267**, 145—172).—β-Ethylthiophen, $\begin{matrix}CEt{:}CH\\ CH{:}CH\end{matrix}\!\!>\!S$, was prepared by distilling a mixture of anhydrous sodium ethylsuccinate and phosphorus trisulphide (compare Damsky, Abstr., 1887, 237). It is a colourless, mobile, highly refractive liquid of sp. gr. 1·0012 at 16°; it boils at 135—136°, has an odour like that of benzene, and is miscible with alcohol, ether, benzene, light petroleum, and chloroform, but insoluble in water. It burns with a very smoky flame, gives a greenish-blue coloration with sulphuric acid and isatin, and is gradually decomposed by concentrated sulphuric acid at the ordinary temperature; it is decomposed by hot dilute nitric acid, and with very concentrated acid an explosively violent reaction takes place. The *bromo*-derivative, C_6H_7BrS, is obtained when the

theoretical quantity of bromine is gradually added to water containing ethylthiophen in suspension; it is a colourless liquid, boils at 180—190°, and dissolves freely in alcohol, ether, chloroform, and light petroleum. The *dibromo*-derivative, $C_6H_6Br_2S$, prepared in like manner, is a yellow oil boiling at 215—225°. The *tribromo*-derivative, $C_6H_5Br_3S$, is formed when ethylthiophen is treated with three times the theoretical quantity of bromine at the ordinary temperature; it is a heavy, yellow oil, boils at 272—280°, and is only slightly volatile with steam. The *pentabromo*-derivative, $C_5H_3Br_5S$, can be obtained by treating ethylthiophen with bromine at 100°; it crystallises from alcohol in yellowish, lustrous needles, melts at 86°, and is insoluble in water, and only sparingly soluble in cold alcohol, but more readily in hot alcohol, ether, chloroform, and light petroleum.

Acetyl-β-ethylthiophen, $\begin{matrix}\text{CEt:CAc}\\ \text{CH : CH}\end{matrix}\!>\!\text{S}$, prepared by treating a solution of ethylthiophen in light petroleum with acetic chloride and aluminium chloride, is a colourless liquid, boils at 227°, is volatile with steam, and darkens in colour on exposure to the air; on oxidation with potassium permanganate in well-cooled alkaline solution, it yields only very small quantities of a dicarboxylic acid. Its *oxime*, $C_8H_{11}NOS$, separates from alcohol in lustrous, prismatic crystals, melts at 56°, and is readily soluble in alcohol, ether, light petroleum, chloroform, and benzene, but insoluble in water.

When acetyl-β-methylthiophen (b. p. 218°), prepared by the method described by Demuth (Abstr., 1886, 228), is oxidised with potassium permanganate in alkaline solution, it is converted into β-methylthiophencarboxylic acid and αβ-thiophendicarboxylic acid; the mixture of the two acids is treated with sufficient soda to convert the dicarboxylic acid into its sodium hydrogen salt, and the monocarboxylic acid is then extracted with ether.

β-Methylthiophen-α-carboxylic acid melts at 140°; Demuth (*loc. cit.*) gives 144° as the melting point of this compound. The *silver* salt, $C_6H_5AgO_2S$, separates from hot water in small, colourless, lustrous crystals. The *lead* salt, $(C_6H_5O_2S)_2Pb$, is a colourless powder.

αβ-Thiophendicarboxylic acid, $C_6H_4O_4S$, crystallises from water in long, colourless, lustrous needles, melts at 270° with decomposition, and is only sparingly soluble in cold water, but very readily in ether; it is identical with the acid prepared by Grünewald (Abstr., 1888, 48) by the oxidation of αβ-dimethylthiophen. The *sodium hydrogen* salt, $C_6H_3O_4SNa + 3H_2O$, separates from water in colourless, star-like forms.

Dibromo-β-methylthiophen, $C_5H_4Br_2S$, prepared as described in the case of the corresponding β-ethyl derivative, is a heavy, yellow oil boiling at 220—230°.

Bromacetyl-β-methylthiophen, C_7H_7OBrS, is formed when a light petroleum solution of the dibromo-derivative is treated with acetic chloride (2 mols.) and aluminium chloride; in this reaction some of the acetic chloride seems to be converted into bromacetic chloride. It is a yellow liquid, darkens in colour on exposure to the air, and is readily soluble in alcohol and ether. Its *oxime*, C_7H_8NOBrS, forms

yellowish crystals, melts at 105°, and is readily soluble in alcohol and ether, but only sparingly in light petroleum, and insoluble in water.

Bromothiophendicarboxylic acid, $C_6H_3O_4BrS$, is obtained when the preceding compound is oxidised with an alkaline solution of potassium permanganate. It separates from hot water in colourless, microscopic, hair-like crystals, sinters together and decomposes at 240°, and is only sparingly soluble in boiling water; when heated with resorcinol, it gives a brown mass, the solution of which in soda is yellowish-red, and shows a green fluorescence. The *lead* salt, C_6HBrO_4SPb, is a colourless powder, insoluble in water. The *silver* salt, $C_6HBrO_4SAg_2$, is very sparingly soluble in water. F. S. K.

Nitrogenous Derivatives of Thiophen and Furfuran. By P. Douglas (*Ber.*, **25**, 1311—1314).—*Thiophen nitrile*, $C_4SH_3{\cdot}CN$, is obtained when crude thiënylglyoxylic acid is boiled with an excess of a concentrated solution of hydroxylamine hydrochloride; it boils at 192°, and is converted into ethoximidothiophen hydrochloride when dry hydrogen chloride is passed through its alcoholic solution.

Ethylthiophenhydroximic acid is produced when ethoximidothiophen is heated with $1\frac{1}{2}$ times its weight of hydroxylamine hydrochloride in aqueous alcoholic solution; when crystallised from water, it melts at 67°, and appears to exist in one modification only, which is probably the anti-compound, $C_4SH_3{\cdot}\overset{\overset{\displaystyle N{\cdot}OH}{\|}}{C}OEt$.

Furfuronitrile, $C_4OH_3{\cdot}CN$, is formed when furfuraldehyde is gently heated with neutral hydroxylamine solution, and the crystalline product obtained by extraction with ether is warmed with acetic anhydride, neutralised, and driven over with steam; it boils at 147° as stated by Wallach (Abstr., 1881, 715).

When the last compound is dissolved in alcohol, and the cooled solution treated cautiously with dry hydrogen chloride, the residue remaining, after treatment with aqueous sodium carbonate, yields on crystallisation from alcohol a white compound which is perhaps ethoximidofurfuran.

Thiopyromucamide, $C_4OH_3{\cdot}CS{\cdot}NH_2$, is produced when furfuronitrile is dissolved in an equal quantity of alcohol and twice its volume of dry ether, and dry hydrogen sulphide passed through. On gently heating, and adding 25 per cent. ammonia, yellowish crystals separate; the pure compound melts at 127°, and is only slightly soluble in cold water, but readily so in alcohol. Furfuronitrile gives with hydroxylamine a crystalline amidoxime melting at about 70°. A. R. L.

Silver Phenylacetylide. By C. Liebermann and F. Damerow (*Ber.*, **25**, 1096—1098).—It is shown that the formula $2(CPh{:}CAg) + Ag_2O$ for this substance given in the text-books is based on an error in Glaser's calculations. Properly calculated, his analytical data correspond with the formula $CPh{:}CAg$. Reason is also given for supposing that silver and copper acetylides have respectively the constitution C_2Ag_2 and C_2Cu_2, the low results obtained on analysing these compounds being due to the presence of moisture.

A compound of silver phenylacetylide with silver nitrate, CPh:CAg + $AgNO_3$, was prepared by adding an alcoholic solution of silver nitrate to an alcoholic solution of phenylacetylene. At first an amorphous precipitate of Glaser's silver phenylacetylide is formed, but this soon changes into pretty, white needles of the silver nitrate compound. This substance was thus obtained in a neutral solution, whereas Glaser obtained silver phenylacetylide in an ammoniacal solution. The silver nitrate compound is actually decomposed by ammonia into silver nitrate and silver phenylacetylide.

C. F. B.

Aromatic Isocyanates. By L. Gattermann and A. Cantzler (*Ber.*, **25**, 1086—1091; compare Abstr., 1890, 970).—When a concentrated aqueous solution of potassium cyanate, and then finely-divided copper, are added to a solution of diazotised aniline, phenyl cyanate is formed, but only in small quantity; it may be extracted with chloroform. Orthotolyl cyanate, boiling at 184—187°, can be made in the same way, and the yield is much better. It reacts like phenyl cyanate, yielding di-substituted carbamides with aniline, toluidine, &c.; whilst if warmed with orthocresol, it yields *orthotolyl orthotolylcarbamate*, $C_6H_4Me{\cdot}NH{\cdot}COO{\cdot}C_6H_4Me$, which crystallises from acetic acid in colourless needles, melts at 126°, and is decomposed into its constituents when heated. Heated at 160° with β-naphthol in a sealed tube, orthotolyl cyanate yields *β-naphthyl orthotolylcarbamate*, $C_6H_4Me{\cdot}NH{\cdot}COO{\cdot}C_{10}H_7$, which crystallises from acetic acid in colourless plates melting at 149°. Heated on the water-bath with benzyl alcohol, orthotolyl cyanate yields *benzyl orthotolylcarbamate*, $C_6H_4Me{\cdot}NH{\cdot}COO{\cdot}CH_2Ph$, which crystallises from light petroleum in colourless needles, and melts at 83—84°. Heated with resorcinol at 120°, *metaphenylene orthotolylcarbamate*, $(C_6H_4Me{\cdot}NH{\cdot}COO)_2C_6H_4$, is formed; this crystallises from alcohol in colourless plates melting at 153—154°. Heated with quinol at 150°, *β-phenylene orthotolylcarbamate*, $(C_6H_4Me{\cdot}NH{\cdot}COO)_2C_6H_4$, is formed; it crystallises from acetic acid in long needles melting at 206·5°. Heated at 125° with benzoïn, a substance $C_6H_4Me{\cdot}NH{\cdot}COO{\cdot}CHPh{\cdot}COPh$ is obtained which crystallises from dilute alcohol in colourless prisms melting at 125°, and is decomposed by heat into its constituents. Heated at 125° with benzamide, *benzoylorthotolylcarbamide*, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}NHBz$, is formed; it crystallises from acetic acid in long needles melting at 210°.

Metatolyl cyanate, boiling at 195—198°, can be obtained in the same way as the ortho-compound, but the yield is smaller. With metatoluidine, it yields *dimetatolylcarbamide*, $CO(NH{\cdot}C_6H_4Me)_2$, melting at 203°, and crystallising from acetic acid in colourless needles.

Metaxylyl cyanate, boiling at 205°, was prepared in a similar manner from symmetrical metaxylidine [1 : 3 : 5]. With xylidine, it yields *dixylylcarbamide*, $CO(NH{\cdot}C_6H_3Me_2)_2$, melting at 250—251°, and crystallising from acetic acid in long, colourless needles.

Pseudocumyl cyanate, boiling at 225—230°, yields, with pseudocumidine, *dipseudocumylcarbamide*, $CO(NH{\cdot}C_6H_2Me_3)_2$, melting at 274°.

Parabromophenyl cyanate, boiling at 215—220°, can be obtained from parabromaniline, but the yield is small. With aniline, it yields *bromodiphenylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br$, crystallising from acetic acid in silvery plates which begin to sublime at 180°.

When diazotised metanitroparatoluidine reacts with potassium cyanate and copper powder, an oil is formed which explodes when distilled. It is, doubtless, nitrotolyl cyanate, for with nitrotoluidine it yields dinitrotolylcarbamide melting at 235°.

Parethoxyphenyl cyanate, boiling at 230—235°, is obtained from paraphenetidine, and unites with it to form *diethoxydiphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}OEt)_2$, which crystallises from acetic acid in long needles melting at 225—226°. The substance described as this cyanate by Köhler (Abstr., 1884, 1159) was probably not a cyanate at all, and was possibly the carbamide.

The method of obtaining cyanates from the diazotised amine, potassium cyanate, and copper powder does not give a yield of more than 20—30 per cent. of the theoretical, except in the case of orthotolyl compounds, when the yield is much greater. C. F. B.

Composition of Betel Oil. By Schimmel (*Chem. Centr.*, 1892, i, 92; from *Schweiz. Wochenschr. Pharm.*, **29**, 402—403).—The oil has a golden-yellow colour and the peculiar odour of betelphenol (Abstr., 1889, 863), and has a density of 1·044 at 15°. The phenol boils at 128—129° under a pressure of 11 mm. The oil, as obtained from different sources, has been found to contain betelphenol in every case, and, in addition, that from Java contained terpenes and chavicol, that from the dried leaf from Siam, a sesquiterpene, whilst that from Manilla contained no other phenol. J. W. L.

Quinitol, the Simplest Sugar of the Inositol Group. By A. v. Baeyer (*Ber.*, **25**, 1036—1040).—Paradiketohexamethylene can be easily prepared in almost any quantity by hydrolysing ethyl succinosuccinate with dilute sulphuric acid; on reduction with sodium amalgam in carbonic acid solution, it is converted into a glycol, which seems to consist of the two theoretically possible geometric forms. The more sparingly soluble portion of this glycol gives a crystalline diacetyl derivative, $OAc{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CH{\cdot}OAc$, melting at 105—106°, from which, by hydrolysing with barium hydroxide, the glycol can be obtained in a pure condition. The compound prepared in this way is probably *cistransparadihydroxyhexamethylene*, and in its appearance and behaviour it resembles a sugar of the mannitol group; its solution is stable towards potassium permanganate in the cold, and does not reduce Fehling's solution even on warming; it crystallises from alcohol in crusts, melts at 143—145°, sublimes and distils without decomposition, and is readily soluble in alcohol and water. The taste of the solid glycol is sweet at first, afterwards bitter; when warmed with potassium dichromate and sulphuric acid, it yields quinone. The author names the compound *quinitol*.

Phloroglucinol is reduced by sodium amalgam, although more slowly than paradiketohexamethylene.

When quinitol is warmed with concentrated hydrobromic or hydriodic acid, it is converted into a crystalline bromide, or iodide, which, on treatment with alcoholic potash, yields a peculiarly-smelling hydrocarbon—in all probability dihydrobenzene—and, on boiling with dilute sulphuric acid, gives a substance having an odour recalling that of oil of turpentine; by the reduction of these halogen compounds, hexamethylene will doubtless be obtained. From the chlorhydrin, or from the hydroxyketone formed as an intermediate product in the reduction of the diketone, it will doubtless be possible to prepare hydroxy- and keto-hexamethylene, compounds corresponding with menthol and menthone, and tetrahydrobenzene, the parent substance of menthene, is also attainable in this way.

Of particular interest, because of their relationship to the terpenes, are the paralkyl derivatives of quinitol, which can, no doubt, be obtained without much difficulty; it is only necessary to prepare ethyl dimethylsuccinosuccinate from ethyl glutarate, in order to obtain dimethylquinitol. From a mixture of ethyl methylsuccinate and ethyl isopropylsuccinate, it will, presumably, be possible to prepare ethyl methylisopropylsuccinosuccinate, and from the latter, methylisopropylquinitol and dihydrocymene.

The nitrile of dihydroterephthalic acid has been prepared from the additive product of the diketone and hydrogen cyanide; it is decomposed by alcoholic potash, yielding benzonitrile and hydrogen cyanide, just as pinylamine gives cymene and ammonia.

Experiments are in progress with the object of preparing all the theoretically possible paradialkyldihydrobenzene derivatives. The methyl ketone of terephthalic acid (paracetylacetophenone), for example, can be easily obtained from the product of the interaction of terephthalic chloride and ethyl sodiomalonate, and this compound must, on reduction, yield paradiethylbenzene; it may be presumed, therefore, that, starting from the five isomeric dihydroterephthalic acids, the five theoretically possible paradiethyldihydrobenzenes can be prepared in like manner.

The hexahydroisophthalic acid, prepared by reducing isophthalic acid, is identical with the compound obtained by Perkin (Trans., 1891, 798) from ethyl pentantetracarboxylate. F. S. K.

Decomposition Products of Anilic Acid. By A. Hantzsch (*Ber.*, **25**, 827—841).—This paper is an answer to Nef's criticisms on the author's work, and contains a theoretical consideration of the experiments described in the following paper. The electrical conductivity of some of the compounds prepared is also given.

E. C. R.

Action of Halogens on Chloranilic and Bromanilic Acids. By H. Landolt, Jun. (*Ber.*, **25**, 842—859).—The silver salt of chloranilic acid, when treated with chlorine in the absence of water, yields tetrachlorotetraketohexamethylene; treated with aqueous hypochlorous acid, it yields trichlorotetraketohexamethylene. The tetrachlorketone yields with alkali, tetrachlorodiketopentamethylenehydroxycarboxylic acid; the trichlorketone yields trichlorodiketopentamethylenehydroxycarboxylic acid. The latter is also formed by the

action of sodium hypochlorite (1 mol.) on chloranilic acid; the former from sodium hypochlorite (2 mols.) and chloranilic acid. The trichlorinated acid is converted by salts of hypochlorous acid into tetrachlorodiketopentamethylenehydroxycarboxylic acid, and by chlorine into trichlorotriketopentamethylene, which is also obtained by the direct action of chlorine on chloranilic acid in aqueous solution.

The action of bromine on bromanilic acid is somewhat different. The compounds obtained are less stable, and the brominated hydroxycarboxylic acids of pentamethylene are not stable, but split up into carbonic anhydride, hydrogen bromide, and the brominated ketone of the pentamethylene ring. Instead of tetrabromodiketopentamethylenehydroxycarboxylic acid, there is formed tribromotriketopentamethylene, and, instead of tribromodiketopentamethylenehydroxycarboxylic acid, there is formed dibromotriketopentamethylene. Silver bromanilate, in the absence of water, yields tetrabromotetraketohexamethylene; in the presence of water, it yields tribromotetraketohexamethylene. From the tetrabromotetraketone, there is formed tribromotriketopentamethylene, and from the tribromotetraketone, there is formed dibromotriketopentamethylene. Tribromotriketopentamethylene is also formed by the direct action of bromine on bromanilic acid, and from dibromotriketopentamethylene by the action of bromine-water.

Trichlorotetraketohexamethylene hydrate, $C(OH)_2<\begin{matrix}C(OH):CCl\\CCl_2 - CO\end{matrix}>CO$ or $C(OH)_2<\begin{matrix}CO\cdot CHCl\\CCl_2-CO\end{matrix}>CO$, is obtained by treating chloranilic acid with an aqueous solution of hypochlorous acid. The aqueous solution is extracted with ether, the ethereal extract dried with anhydrous copper sulphate, evaporated in a vacuum, and the residue washed with benzene and crystallised from a mixture of benzene and ether. It is easily soluble in ether and alcohol, somewhat easily so in water, melts at 158° with decomposition, is acid to litmus, and is insoluble in concentrated sulphuric acid. When reduced by warming with sulphurous acid or sodium thiosulphate, it is converted into chloranilic acid. The *azine*, $C_6(OH)_3Cl_3{:}N_2{:}C_6H_4$, is obtained as a metallic, orange precipitate, by adding orthophenylenediamine hydrochloride to a dilute solution of the trichlorketone. It quickly turns red in the air, and melts at 117°.

Trichlorodiketopentamethylenehydroxycarboxylic acid is obtained by treating the above trichlorketone with cold concentrated sodium carbonate, and, after some time, acidifying with sulphuric acid, and extracting with ether. It melts at 170°, and contains ether of crystallisation. It may also be obtained from the trichlorketone by the action of dilute sodium hydroxide or ammonia. When treated with hypochlorous acid (1 mol.), it is converted into trichlorotriketopentamethylene, which, on treatment with alcoholic ammonia, yields a characteristic ammonium salt melting at 207°.

Trichlorotriketopentamethylene is also obtained by the action of chlorine-water on chloranilic acid, and, in small quantities, by the action of 1 mol. of hypochlorous acid. It is the final product of the action of chlorine or hypochlorous acid on chloranilic acid in the

absence of alkali. When treated with twice the theoretical quantity of phenylhydrazine acetate, it yields a *trihydrazine*,

$$C_5H_2Cl_2(N_2HPh)_3 + 2H_2O,$$

with evolution of hydrogen chloride.

Tetrachlorotetraketohexamethylene, $CCl_2<\begin{matrix}CO\cdot CO\\CO\cdot CO\end{matrix}>CCl_2$, is obtained by the action of dry chlorine on silver chloranilate suspended in carbon bisulphide. It melts about 60°, and is easily decomposed by water, yielding carbonic anhydride, hydrogen chloride, and trichlorotriketopentamethylene. When the freshly-prepared tetrachlorotetraketone is treated with cold concentrated soda, it yields a colourless solution, from which, by acidifying and extracting with ether, the hydrate of *tetrachlorodiketopentamethylenehydroxycarboxylic acid* is obtained. The latter crystallises in beautiful, white needles, melts at 217°, and yields an ammonium salt melting at 145°.

Tribromotetraketohexamethylene is obtained by the action of bromine vapour on an aqueous solution of the acid sodium salt of bromanilic acid. It is separated by acidifying with sulphuric acid and extracting with ether, and is identical with the substance formerly described by Hantzsch as bromanilic acid bromide (*Ber.*, **21**, 2438). It is very easily converted into equivalent quantities of bromanilic acid and tribromotriketopentamethylene. With excess of bromine, it yields tribromotriketopentamethylene, and with sulphurous acid it gives a quantitative yield of bromanilic acid. The *azine*, $OH\cdot C_6Br_2O:N_2:C_6H_4$, is obtained as a reddish-brown precipitate on adding phenylenediamine hydrochloride and sodium acetate to a concentrated aqueous solution of the tribromide. The *hydrazone*, $C_6OBr_2(N_2HPh)_3 + 2H_2O$, is obtained as an amorphous, brownish-red precipitate.

Dibromotriketopentamethylene hydrate is obtained by dissolving tribromotetraketohexamethylene in soda, acidifying with sulphuric acid, and extracting with ether. It crystallises with $\frac{1}{2}$ mol. of ether in beautiful prisms; when exposed to the air, it loses its ether and forms a colourless oil, which cannot be obtained crystalline except from ether. It has an acid reaction, but easily loses hydrogen bromide in aqueous or alkaline solution. When treated with excess of hypochlorous acid in the presence of hydrochloric acid for some hours at the ordinary temperature, it yields dichlorobromacetone, $CO(CCl_2Br)_2$ (m. p. 53°), and oxalic acid.

Tribromotriketopentamethylene is obtained by adding an excess of bromine to an aqueous solution of dibromotriketopentamethylene, then at once adding sulphurous acid until the mixture is colourless and extracting with ether. It melts at 189°, yields an ammonium salt melting at 183°, and can be sublimed undecomposed by careful heating. With phenylhydrazine, it yields a compound of the formula $C_5H_2Br_2(N_2HPh)_3 + 2H_2O$.

If an excess of bromine is allowed to act for some time on dibromotriketopentamethylene, perbromacetone, $CO(CBr_3)_2$, and oxalic acid are formed.

Tribromotriketopentamethylene is also formed by treating tetrabromotetraketohexamethylene with well-cooled soda solution.

E. C. R.

Preparation of Orthonitraniline. By C. Turner (*Ber.*, **25**, 985—987).—Orthonitraniline may be readily prepared according to the following method:—50 grams of acetanilide is heated on the water-bath with 150 grams of fuming sulphuric acid containing 20 per cent. of SO_3 until the whole is soluble in alkalis, 100 grams of concentrated sulphuric acid added to the cooled mixture, and afterwards the theoretical quantity of nitric acid mixed with an equal volume of sulphuric acid, the temperature not being allowed to rise above 0°. After nitration, 140 c.c. of water is added, so that a sulphuric acid of about 67 per cent. strength is formed, and the whole heated to the boiling point; the boiling is continued for half an hour after complete solution has taken place, and the nitraniline separated from the cooled liquid by fractional precipitation with water. The first portions are somewhat impure, but the subsequent fractions are sufficiently pure for most purposes; they may, however, be further purified by recrystallisation or distillation in a current of superheated steam. The yield is about 70 per cent. of the theoretical.

Orthonitraniline is not affected by boiling with ammonium sulphide for several hours, but is readily reduced by tin and hydrochloric acid; from the product, orthodiamidobenzene may be isolated in the usual manner. H. G. C.

Anhydro-compounds. By S. Niementowski (*Ber.*, **25**, 860—875).—Ethenyldiamidotoluene is best prepared by reducing metanitroparacetotoluidide with the theoretical quantity of tin and hydrochloric acid (1 concentrated acid to 1 water); the tin is precipitated with hydrogen sulphide, the filtrate evaporated, and the hydrochloride of the base decomposed with ammonia or soda. It crystallises from dilute spirit, and melts at 203°.

Bromethenyldiamidotoluene is obtained by brominating ethenyldiamidotoluene dissolved in acetic acid or carbon bisulphide and decomposing with alkali the hydrobromide thus obtained. It crystallises from dilute spirit in white needles, melts at 216°, is easily soluble in alcohol and acetone, less so in ethyl acetate, sparingly in benzene and chloroform, and almost insoluble in hot water and carbon bisulphide. It is not attacked by potassium hydroxide, sodium and amyl alcohol, or tin and hydrochloric acid. Its alcoholic solution, when boiled with silver nitrate, gives no precipitate of silver bromide. The author puts forward the following formulæ for this compound:—

$$\begin{matrix} CMe\cdot CBr{:}C-N \\ \| \quad\quad | \\ CH-CH{:}C\cdot NH \end{matrix} \gg CMe \text{ and } \begin{matrix} CMe\cdot CH{:}C-N \\ \| \quad\quad | \\ CBr\cdot CH{:}C\cdot NH \end{matrix} \gg CMe.$$

The *hydrochloride* crystallises with 2 mols. H_2O in long, hard needles, and has no sharp melting point. The *hydrobromide* is similar to the hydrochloride, but is less soluble. The *nitrate* crystallises without water, and decomposes at 228°.

Nitrobromethenyldiamidotoluene is obtained by gradually adding bromethenyldiamidotoluene (12 grams) to fuming nitric acid (50 grams sp. gr. = 1·53); the mixture is boiled for 20 minutes, poured into 15 times the quantity of water, and the nitrate thus obtained hydrolysed with potash. It crystallises from alcohol in yellow needles, melts at 219°, is soluble in ethyl acetate, alcohol, chloroform,

and acetone, less so in boiling benzene and ether, and only very sparingly soluble in boiling water. The *nitrate* melts at 207°, and crystallises in white needles. The *hydrochloride* and *sulphate* are also crystalline.

Metabromorthoacetotoluidide is best prepared by passing a current of air saturated with bromine vapour through a solution of acetotoluidide. (200 grams) in glacial acetic acid (1300 grams) until the solution solidifies. It is obtained pure after one crystallisation from alcohol, and melts at 156—157°. The acetic acid mother liquors contain metabromorthotoluidine hydrobromide. The latter blackens at 260°, decomposes at 280°, and is easily hydrolysed by cold potash.

Metanitrometabromorthoacetotoluidide [Me : NHAc : NO_2 : Br = 1 : 2 : 3 : 5] is obtained by adding finely powdered bromacetotoluidide to four times its weight of nitric acid (1·48), taking care that the temperature does not rise above 25°. After an hour, the product is poured into water, washed, dried, and crystallised from acetic acid. It forms yellowish-white needles, melts at 205°, is soluble in acetic acid, alcohol, acetone, and chloroform, and sparingly so in benzene or hot water. On hydrolysis with potash, it yields nitrobromotoluidine, which may be purified by steam distillation, forms orange-yellow leaflets or needles, and melts at 145°.

Dinitrometabromorthoacetotoluidide is obtained by adding finely-powdered bromacetotoluidide (1 part) to a mixture of sodium nitrate (1 part) and concentrated sulphuric acid (20 parts), and allowing the mixture to remain some time at the ordinary temperature. It crystallises in slender, white needles, melts at 244° with frothing, and is soluble in boiling alcohol, acetic acid, acetone, and ethyl acetate, sparingly so in benzene, toluene, and chloroform, and almost insoluble in water.

Metabromisoethenyldiamidotoluene, $C_6H_2MeBr<^{NH}_{N}>CMe$, is obtained, together with *metabromoxyisoethenyldiamidotoluene*,

$$C_6H_2MeBr<^{NH\cdot CMe}_{N}>O,$$

by the reduction of metabromometanitrorthoacetotoluidide with tin and hydrochloric acid. The hydrochloride of bromoxyisoethenyldiamidotoluene crystallises out in long, white needles, whilst the stannochloride of bromisoethenyldiamidotoluene remains in solution. The latter is decomposed by hydrogen sulphide, and the hydrochloride thus obtained is hydrolysed by suspending it in absolute alcohol, and adding sodium or solid potassium hydroxide.

Bromisoethenyldiamidotoluene melts at 244—246°, crystallises in well-formed, colourless tablets, and is sparingly soluble in organic solvents, and very sparingly so in water. The *hydrochloride* crystallises with 1 mol. of water in needles. The *nitrate* crystallises in slender, white needles, and melts at 217—219° with decomposition.

Metacetotoluidide is nitrated much less readily than its isomeride. The product consists of orthonitrometacetotoluidide (m. p. 102°), a large quantity of oily products, and orthonitrometacresol (m. p. 56°).

E. C. R.

Synthesis of Dehydrothiotoluidine. By L. Gattermann and O. Neuberg (*Ber.*, **25**, 1081—1085). — *Paranitrobenzotoluidide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4Me$, was obtained by mixing ethereal solutions of paranitrobenzoic chloride and paratoluidine. It crystallises from alcohol in yellowish needles melting at 197°. When gently warmed with phosphoric chloride, it yields an *amide chloride*,

$$NO_2 \cdot C_6H_4 \cdot CCl_2 \cdot NH \cdot C_6H_4Me,$$

which crystallises from ether in large, golden needles, melts at 119°, and decomposes in moist air. When a benzene solution of this substance is treated with dry hydrogen sulphide, or an ethereal solution with alcoholic sodium sulphide, and finally acidified, small quantities of *thionitrobenzotoluidide* are formed, and when this substance is allowed to remain with alkaline potassium ferricyanide, it is oxidised to a compound which crystallises from acetic acid in yellowish-red needles, and is reduced by tin or stannous chloride and hydrochloric acid to dehydrothiotoluidine. A slight variation of this method was attained by converting the amide chloride into an amidine, and this, by the action of carbon bisulphide into the thioamide. The amide chloride, when heated with aniline at 150°, yields an amidine, $NO_2 \cdot C_6H_4 \cdot C(NPh) \cdot NH \cdot C_6H_4Me$, which crystallises from alcohol in colourless needles, melting at 260°. With paratoluidine, it yields the amidine $NO_2 \cdot C_6H_4 \cdot C(N \cdot C_6H_4Me) \cdot NH \cdot C_6H_4Me$, which crystallises from alcohol in lustrous crystals melting at 300° with decomposition, and very sparingly soluble in most solvents. When heated with carbon bisulphide at 200°, it yields the thioamide, and this, as described above, can be converted into dehydrothiotoluidine.

The constitution previously assigned (Abstr., 1889, 867) to dehydrothiotoluidine is thus confirmed. C. F. B.

Reduction Products of Azo-compounds. By P. Jacobsen and W. Fischer (*Ber.*, **25**, 992—1012).—In view of the discussion now being carried on as to whether the compounds obtained by the action of diazobenzene chloride on phenols are to be regarded as hydroxyazo-compounds or as quinonehydrazones (compare Abstr., 1890, 614; 1891, 1209), the authors examined the action of reducing agents on an ether of the simplest of such compounds, namely, the ethyl ether of parahydroxyazobenzene, the two possible formulæ of which are as follows :—

$$EtO \cdot C_6H_4 \cdot N{:}N \cdot C_6H_5, \qquad O{:}C_6H_4{:}N \cdot NH \cdot C_6H_5.$$

They have been able to show that aniline and paraphenetidine are among the products of reduction, thus proving the first formula to be correct; these, however, only form a small portion of the products of the reaction, two other substances being obtained, the examination of which has led to very interesting results.

Parethoxyazobenzene was prepared by dissolving hydroxyazobenzene and the requisite quantity of sodium in alcohol, boiling with ethyl bromide for three hours, and subsequently adding a little more sodium and ethyl bromide, and boiling again for two hours; it separates out on pouring the liquid into water, and, after recrystal-

lisation from alcohol, melts at 77—78°, as given also by Bohn (*Inaug. Diss.. Zürich*, 1883). The reduction was carried out with stannous chloride and hydrochloric acid; a resinous stannochloride quickly separates out, more of which may be obtained by the addition of small quantities of water, and if the mother liquors are allowed to remain for some time, another stannochloride separates as a thick, white, crystalline precipitate; the filtrate from this salt contains the aniline and paraphenetidine, which were isolated and identified by their boiling points and conversion into their acetyl derivatives.

The two stannochlorides may be converted into the corresponding bases in the usual manner; the first has the composition $C_{14}H_{16}N_2O$, crystallises from dilute alcohol in long, pale-violet needles, and melts after repeated crystallisation at 95°; the second is isomeric with the first, and will be described later, the first-named base only being discussed in the present paper. This had been previously prepared by the action of ammonium sulphide on parethoxyazobenzene by Bohn (*loc. cit.*), who regarded it as a diphenyl derivative obtained by the usual intramolecular change from the hydrazo-compound first formed; Nölting and Werner take the same view (Abstr., 1891, 211), and the authors at first adopted the same supposition, according to which it would be an ethoxydiphenylene, $C_{12}H_7(NH_2)_2{\cdot}OEt$ [$OEt : (NH_2)_2 = 3 : 6 : 4'$]. They therefore endeavoured to convert it into the corresponding dihydroxy-derivative by the action of nitrous acid and subsequent treatment with water, but, instead of the diazo-compounds, they obtained an azimido-derivative, which, after purification, forms colourless crystals having the composition $C_{14}H_{13}N_3O$ and melting at 107—108°; it has feebly basic properties, is readily soluble in alcohol, ether, and benzene, less readily in light petroleum, and crystallises from acetic acid in lustrous, rectangular tablets. The formation of this compound shows that the above constitution of the base cannot be correct, but that it behaves in a manner similar to the orthodiamido-compounds. This is confirmed by the action of formic acid and acetic anhydride, which yield the *methenyl* and *ethenyl* derivatives characteristic of ortho-diamido-compounds; the former, $C_{15}H_{14}N_2O$, forms colourless, compact crystals, melts at 77—78°, and yields a crystalline nitrate, and the latter, $C_{16}H_{16}N_2O$, is an oil, but also yields a crystalline nitrate. The base further combines with carbon bisulphide, forming a well crystallised derivative, $C_{14}H_{14}\ll^{N}_{N}>CS$, or $C_{14}H_{13}\ll^{N}_{N}\gg C{\cdot}SH$, which separates from alcohol in silky, asbestos-like needles, and melts at 229°.

The formation of these anhydro-compounds may be explained on the supposition that the base is an orthodiamido-compound, or that it is a peridiamidodiphenyl derivative, which might, like diphenic acid (in which the carboxyl groups occupy the peri-position), yield anhydro-derivatives. Peridiamidodiphenyl itself has, however, been prepared by Täuber (Abstr., 1891, 570), and behaves towards nitrous acid and acetic anhydride in the usual manner, yielding diazo- and acetyl compounds and not anhydro-derivatives; the supposition that

in Bohn's base the amido-groups occupy the peri-position is therefore very improbable. It has been shown to be impossible in the following manner:—If the base consists of a diamidodiphenyl, $OEt\cdot C_{12}H_7(NH_2)_2$, it must yield an azimido-compound, and have one of the two following formulæ:—

$$OEt\cdot C_{12}H_7<\begin{matrix}NH\\ -N\end{matrix}>N, \qquad OEt\cdot C_{12}H_7<\begin{matrix}N\\ |\\ N\end{matrix}>NH;$$

in either case the compound would contain a replaceable hydrogen atom, but all attempts to replace it by a methyl or acetyl group have been without success. With methyl iodide, it combines to form a quaternary compound, $C_{14}H_{13}N_3O,CH_3I$, which yields a caustic hydroxide, and on heating at 190°, splits up into methyl iodide and the original azimide, and not its methyl derivative. The azimide can therefore contain no replaceable hydrogen, and must be a tertiary compound containing the group:—

$$\begin{matrix}-NR\\ -N\end{matrix}>N,$$

and the base from which it is formed must contain one imido- and one amido-group.

The formation of a compound containing these two groups from a hydrazo-compound may be imagined as taking place in the following manner:—In the formation of benzidine from hydrazobenzene, a hydrogen atom from each benzene nucleus migrates to the nitrogen atom attached to it, the two benzene residues then uniting together; this may be represented as follows:—

$$\begin{matrix}H\cdot C_6H_4\cdot NH\\ |\\ H\cdot C_6H_4\cdot NH\end{matrix} = \begin{matrix}C_6H_4\cdot NH_2\\ |\\ C_6H_4\cdot NH_2\end{matrix}.$$

If, however, the migration of the hydrogen atom were only to take place in one benzene nucleus, the nitrogen atom in connection with that nucleus would be then separated from the second imido-group, leaving the latter free to unite with the benzene nucleus in the position previously occupied by the hydrogen atom, the change being represented as follows:—

$$\begin{matrix}H\cdot C_6H_4\cdot NH\\ |\\ C_6H_5\cdot NH\end{matrix} = \begin{matrix}C_6H_4\cdot NH_2\\ |\\ C_6H_5\cdot NH\end{matrix}.$$

Such a change has not hitherto been observed with hydrazobenzene itself, but in that case both halves of the molecule are similar, and there is no apparent reason for one half showing any special behaviour; in the case of ethoxyhydrazobenzene, however, the two halves of the molecule are dissimilar, and it is quite possible that such an intramolecular change as represented above might take place; this may occur in two different ways according to the half of the molecule in which the migration of the hydrogen atom takes place:—

$$\begin{matrix} H\cdot C_6H_4\cdot NH \\ | \\ OEt\cdot C_6H_4\cdot NH \end{matrix} = \begin{matrix} C_6H_4\cdot NH_2 \\ | \\ OEt\cdot C_6H_4\cdot NH \end{matrix},$$

$$\begin{matrix} C_6H_5\cdot NH \\ | \\ H\cdot OEt\cdot C_6H_3\cdot NH \end{matrix} = \begin{matrix} C_6H_5\cdot NH \\ | \\ OEt\cdot C_6H_3\cdot NH_2 \end{matrix}.$$

Either of these formulæ would explain the reactions of the base, so far as they are at present known, both formulæ representing a mono-substituted orthodiamidobenzene, which would from analogy yield a methenyl and ethenyl derivative and a tertiary azoimide. In order, however, to obtain more definite evidence on this point, the base was subjected to other reactions in which mono-substituted ortho-diamidobenzene plays a characteristic part. When heated with benzaldehyde and alcohol, it behaves in exactly the same manner as orthamidoditolylamine (Fischer and Lieder, Abstr., 1891, 434), yielding a dihydro-anhydro-compound containing the group $\begin{matrix} NR \\ | \\ NH \end{matrix}>CHPh$, which crystallises in needles, and melts at 152°. It likewise combines with benzoïn to form a dihydroquinoxaline derivative (compare O. Fischer, Abstr., 1891, 747), which crystallises in stellate groups of prisms, melts at 126—128°, and shows a yellowish-green fluorescence in dilute alcoholic solution; with benzil, it behaves like orthamidodiphenylamine (Abstr., 1891, 945, 1109), yielding a fluorescent *azonium* base, which melts at 145°, then quickly solidifies, and remelts on further heating at 162—163°, and on oxidation, like the azonium bases of Fischer and Busch (Abstr., 1891, 1109, 1514), yields the dihydroquinoxaline obtained with benzoïn.

The above reactions characterise the base definitely as a mono-substituted orthodiamido-derivative, and by means of further reactions, which will be described in a subsequent paper, it has been shown that the second of the formulæ given above is correct. These results show conclusively that, besides their conversion into benzidine derivatives, hydrazo-compounds are capable of undergoing another kind of intramolecular change in which bases of the type of amido-diphenylamine are produced. This change probably occurs in other hydrazo-derivatives than the one discussed in this paper, and it is not unlikely that some of the substance hitherto supposed to be benzidine derivatives are in reality derivatives of amidodiphenyl-amine (compare Täuber, this vol., p. 853, and Witt and Schmidt, this vol., p. 862). H. G. C.

Displacement of the Hydrazine Residue by Halogens. By L. Gattermann and R. Hölzle (*Ber.*, **25**, 1074—1075).—It is well known that hydrazines are oxidised by copper sulphate to hydrocarbons; for example, phenylhydrazine to benzene. But if, instead of the free hydrazine, a hot solution of phenylhydrazine in hydrochloric acid is allowed to drop into a boiling aqueous solution of copper sulphate, nitrogen is evolved, metallic copper is deposited, and chlorobenzene distils over with the steam. The yield is 86·4 of the theoretical. Diazobenzene chloride is probably formed as an inter-

mediate product. Bromo-, iodo-, and cyano-benzene may be prepared in a similar manner; the yield is respectively 60, 20, and 10 per cent. of the theoretical. The tolylhydrazines exhibit the same reaction.

C. F. B.

Acid Hydrazides. By L. Gattermann, E. S. Johnson, and R. Hölzle (*Ber.*, **25**, 1075—1081).—Various hydrazides were oxidised by boiling them with a solution of copper sulphate in aqueous ammonia, and the products which separated were purified by boiling out with alcohol.

Formylphenylhydrazine, prepared from formamide and phenylhydrazine, yields *formyldiphenylhydrazine*, $NPh_2{\cdot}NH{\cdot}CHO$, which yields diphenylamine when distilled, and can be synthesised from diphenylhydrazine and formic acid. It melts at 116·5°, crystallises from alcohol in colourless needles, dissolves sparingly in hot water and light petroleum, readily in other solvents. Like all the secondary hydrazides mentioned below, it yields, with strong sulphuric acid, a blue solution which turns green when warmed.

Acetylphenylhydrazine yields *acetyldiphenylhydrazine*, $NPh_2{\cdot}NHAc$, also prepared from diphenylhydrazine and acetic chloride. It crystallises from dilute alcohol in colourless needles melting at 185° (uncorr.).

Propionylphenylhydrazine yields *propionyldiphenylhydrazine*,

$$NPh_2{\cdot}NH{\cdot}COEt,$$

which crystallises from dilute alcohol in colourless needles melting at 178°.

Benzoylphenylhydrazine yields benzoyldiphenylhydrazine,

$$NPh_2{\cdot}NHBz,$$

identical with the substance obtained from diphenylhydrazine and benzoic chloride. It forms colourless needles melting at 189°.

Formylorthotolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}CHO$, was obtained from formamide and orthotolylhydrazine. It crystallises from alcohol in flat, colourless needles, melts at 121°, and, when oxidised, yields *formyldiorthotolylhydrazine*, $N(C_6H_4Me)_2{\cdot}NH{\cdot}CHO$; this crystallises from alcohol in colourless plates melting at 139°.

Acetylorthotolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NHAc$, from acetic acid and orthotolylhydrazine, crystallises from water in colourless plates melting at 104°. It yields *acetyldiorthotolylhydrazine*, $N(C_6H_4Me)_2{\cdot}NHAc$, which crystallises from alcohol in lustrous plates melting at 191°.

Propionylorthotolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}COEt$, from propionic acid and orthotolylhydrazine, crystallises from water in colourless tables melting at 83—84°. It yields *propionyldiorthotolylhydrazine*, $N(C_6H_4Me)_2{\cdot}NH{\cdot}COEt$, which crystallises from dilute alcohol in colourless needles melting at 167°.

Benzoylorthotolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NHBz$, from benzoic chloride and orthotolylhydrazine, forms long, lustrous needles melting at 180°. It yields *benzoyldiorthotolylhydrazine*, $N(C_6H_4Me)_2{\cdot}NHBz$, which crystallises in flat needles melting at 209°.

Formylparatolylhydrazine yields *formyldiparatolylhydrazine*,

$$N(C_6H_4Me)_2{\cdot}NH{\cdot}CHO,$$

which crystallises from dilute alcohol in thin, silky plates, and melts at 146°.

Acetylparatolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NHAc$, from acetic acid and paratolylhydrazine, forms plates melting at 121°. It yields *acetyldiparatolylhydrazine*, $N(C_6H_4Me)_2{\cdot}NHAc$, which crystallises from alcohol in silvery needles melting at 176°.

Propionylparatolylhydrazine, $C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}COEt$, crystallises from water in flat needles melting at 170°. It yields *propionyldiparatolylhydrazine*, $(C_6H_4Me)_2N{\cdot}NH{\cdot}COEt$, which crystallises from dilute alcohol in small needles melting at 171·5°.

Benzoylparatolylhydrazine yields benzoyldiparatolylhydrazine, already prepared from diparatolylhydrazine and benzoic chloride.

Chloracetylphenylhydrazine, $NHPh{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, is obtained from chloracetic chloride and phenylhydrazine. It crystallises from ether in ill-defined crystals melting at 115°. It is decomposed by water, and consequently does not suffer oxidation in the normal manner.

When the product obtained from ethyl chloroformate and phenylhydrazine is oxidised, it yields a substance, $NPh_2{\cdot}NH{\cdot}COOEt$, which crystallises from alcohol in long, colourless needles melting at 140°.

C. F. B.

Phenyldithiobiuret. By E. Fromm (*Ber.*, **25**, 1277—1281).—The compounds obtained by the interaction of ketones with thiobiurets, in molecular proportion, in the presence of hydrogen chloride are named by the author *thioketurets*. *α-Phenyldithiodimethylketuret*, $C_{11}H_{13}N_3S_2$, is produced from acetone and α-phenyldithiobiuret; it melts at 239°, contains 2 atoms of hydrogen displaceable by metal, and therefore dissolves in alkalis; the *dibenzyl* derivative, $C_{25}H_{25}N_3S_2$, melts at 128°, and when boiled with concentrated hydrochloric acid decomposes into ammonia, aniline, acetone, and *benzyl imidodicarbothioxylate*, $HN(COSCH_2Ph)_2$; the last-mentioned compound melts at 146°, and, when treated with alkalis, decomposes into benzyl mercaptan and ammonia. These facts are most easily explained by assigning to α-phenyldithiodimethylketuret the constitution $NPh{:}C(SH){\cdot}N{<}\begin{matrix}CMe_2\\C(SH)\end{matrix}{>}N$.

A. R. L.

Orthohydroxyacetophenone. By Y. Tahara (*Ber.*, **25**, 1306—1310).—*Ethyl orthomethoxybenzoylacetate*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}COOEt$ [= 1 : 2], is obtained when methyl ethylsalicylate (50 grams) is mixed with ethyl acetate (24·5 grams) and sodium wire (6·4 grams) added; after adding alcohol (about 2 grams), the reaction becomes brisk, and the mixture is heated on the water-bath for 18 hours. The mass, after cooling, is treated with water, and the aqueous solution extracted with ether, the crude product being fractionally distilled under diminished pressure, and further purified by means of its sodium hydrogen sulphite compound. It is a colourless oil of an aromatic odour, and is sparingly soluble in water, readily in ether; its alcoholic solution gives a red colour with ferric chloride.

Orthomethoxyphenylphenylpyrazolone, $OMe{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}CH_2{\cdot}CO\\|\\N-NPh\end{matrix}$, separates when the last compound and phenylhydrazine are dissolved in

acetic acid and the solutions mixed; it melts at 114°, and is very little soluble in water; its alcoholic solution is coloured reddish-brown by ferric chloride,

Orthomethoxybenzoylacetic acid is obtained by allowing a solution of the above ethyl salt in dilute sodium hydroxide to remain for three days. It is precipitated by sulphuric acid, purified by redissolving in sodium carbonate and reprecipitating with acid, and finally crystallised from dilute alcohol; it crystallises in tables, melts at 68° with decomposition, and is sparingly soluble in water; it gives a red colour with ferric chloride; the silver salt crystallises in prisms.

Orthomethoxyacetophenone. $OMe{\cdot}C_6H_4{\cdot}COMe$, is produced by boiling ethyl orthomethoxybenzoylacetate with dilute sulphuric acid for 10 hours; it is an oil having a faint odour, boils at 240° (712 mm.), and is insoluble in alkalis; the phenylhydrazine compound crystallises in colourless leaflets, and melts at 86°.

Orthohydroxyacetophenone is prepared by heating the last compound with concentrated hydrochloric acid in a sealed tube at 130°. It is a colourless oil having a strong phenolic odour, boils at 213° (717 mm.), is sparingly soluble in water, but miscible in all proportions with ether, alcohol, and glacial acetic acid, and is coloured violet-red by ferric chloride. The *phenylhydrazone* crystallises from alcohol in delicate needles, and melts at 107°; whilst the *acetyl* derivative forms colourless leaflets, and melts at 89°. A. R. L.

Derivatives of Cyanacetophenone. By F. Garelli (*Gazzetta*, **22**, i, 140—146).—Claisen (Abstr., 1892, 506), by distilling phenylisoxazolic acid, obtained small quantities only of cyanacetophenone. Salvatori, however (Abstr., 1892, 304), found the yield to be satisfactory, and this is confirmed by the author, who obtained about 66 per cent. of the theoretical.

Cyanacetophenone (4 grams) dissolved in absolute alcohol (300 c.c.) is reduced by sodium with production of phenylpropylamine. The alcohol is distilled off, and the crude base purified by steam distillation and conversion into its hydrochloride. Small quantities of acetic and benzoic acids are also formed during the reduction. Phenylpropylamine oxalate melts at about 190° with decomposition; the low melting point observed by Tafel (Abstr., 1886, 939; 1889, 975) is probably due to the presence of dioxalate as an impurity in the normal salt. The *picrate* crystallises in long, yellow needles, and melts at 152—153° without decomposition; it is soluble in boiling water, sparingly so in cold water. W. J. P.

Dehydrodiacetylpæonol. By W. N. Nagai (*Ber.*, **25**, 1284—1291; compare this vol., p. 58).—When pæonol (20 grams) is boiled in a reflux apparatus for 16 hours with acetic anhydride (40 grams) and fused sodium acetate (20 grams), the product triturated with ether, repeatedly boiled with 18 per cent. acetic acid, which extracts an *acetylpæonol* (m. p. 130°), and crystallised from alcohol, yellowish leaflets of a compound melting at 160° are obtained. It has the composition $C_{13}H_{12}O_4$, and may be provisionally named dehydrodiacetylpæonol; it is readily soluble in chloroform, sparingly in hot benzene,

and insoluble in alkalis and ammonia. When the new compound is heated on the water-bath for a short time with half its weight of potassium hydroxide and a little alcohol, potassium acetate and the salt $C_{11}H_{11}O_4K$ are formed; the latter, when treated in aqueous solution with dilute mineral acids, yields *hydroxyacetylpæonol*, $C_{11}H_{12}O_4$, a compound crystallising in colourless needles melting at 68°, and decomposing into pæonol, acetic acid, and paramethoxysalicylic acid (m. p. 158°) when boiled with alkalis; its alcoholic solution gives a violet colour with ferric chloride. The same products are obtained when dehydrodiacetylpæonol is heated on the water-bath with aqueous or alcoholic potash for 30 minutes.

Dehydracetylpæonol, $C_{11}H_{10}O_3$, is produced by boiling the last-mentioned hydroxy-compound with dilute hydrochloric acid, or dehydrodiacetylpæonol with sodium carbonate; it forms colourless prisms, melts at 113°, and is sparingly soluble in cold water.

Dehydromethylacetylpæonol, $C_{12}H_{12}O_3$, is obtained by the interaction of potassium hydroxyacetylpæonol and methyl iodide; it crystallises from dilute alcohol in colourless needles, melts at 126°, and is sparingly soluble in water. *Isomethylpæonol*, $C_{10}H_{12}O_3$, is formed when the last compound is boiled with alkalis; it possesses the characters of a phenol, gives a reddish-violet colour with ferric chloride, crystallises in colourless, rhombic prisms, and melts at 58°. On boiling the above-mentioned diacetylpæonol (m. p. 130°) with alcoholic potash, it yields a compound melting at 159°, which is perhaps identical with Duisberg and v. Pechmann's β-methylumbelliferone methyl ether (Abstr., 1884, 66; compare following abstract). A. R. L.

Constitution of Dehydrodiacetylpæonol and of Dehydrodiacetylresacetophenone. By Y. Tahara (*Ber.*, **25**, 1292—1305). —From his own experiments, as well as those of Nagai (last abstract), the author concludes that the constitution of "dehydrodiacetylpæonol" is $OMe\leqslant\begin{matrix}CH_2\text{—}C(:CH\cdot COAc)\\ CH\cdot CH:C\cdot CO\cdot CH\end{matrix}$, and that of "dehydrodiacetylresacetophenone" $OH\cdot C\leqslant\begin{matrix}CH_2\text{—}C(:CH\cdot COAc)\\ CH\cdot CH:C\cdot CO\cdot CH\end{matrix}$.

"Isomethylpæonol," obtained by Nagai (*loc. cit.*), forms a *phenylhydrazone*, $C_{10}H_{12}O_2{:}N_2HPh$, which crystallises in long, colourless prisms and melts at 101°; it is found to be identical with hydroxymethoxyphenyl ethyl ketone, $OH\cdot C_6H_3(OMe)\cdot COEt$ [1 : 2 : 4], described by Goldzweig and Kaiser (*J. pr. Chem.* [2], **43**, 90). *Dehydrodiacetylpæonol phenylhydrazone*, $C_{13}H_{12}O_3{:}N_2HPh$, crystallises in short prisms, melts at 213°, and gives *dehydracetylpæonol phenylhydrazone*,

$$C_{11}H_{10}O_2{:}N_2HPh,$$

melting at 206°, when boiled with alcoholic potash; the latter is a phenolic compound, and yields a methyl derivative melting at 150°.

Bromodehydracetylpæonol, $C_{11}H_9BrO_3$, formed by brominating dehydracetylpæonol in ethereal solution, melts at 175—177°, and gives dehydracetylpæonol on treatment with alkali. Diacetylresorcinol (Nencki and Sieber, Abstr., 1881, 591) is obtained by mixing resaceto-

phenone and fused sodium acetate (equal parts) with acetic anhydride (2 parts) at the ordinary temperature; when, however, the mixture is boiled for some hours, acetyldehydrodiacetylresacetophenone, $C_{14}H_{12}O_5$, which crystallises in colourless prisms and melts at 127°, is formed; the latter, on treatment with dilute ammonia, yields dehydrodiacetylresacetophenone, $C_{12}H_{10}O_4$, which crystallises in silky needles and melts at 182°. When the last compound is boiled with sodium carbonate solution, dehydracetylresacetophenone, $C_{10}H_8O_3$, is obtained; it crystallises in colourless, rhombic prisms and melts at 250°; the same compound is produced when dehydrodiacetylpæonol is heated in a sealed tube with hydrochloric acid at 160° for five hours.

The author shows that the diacetylpæonol melting at 130° (last abstract) is α-acetyl-β-methylumbelliferone methyl ether, and consequently the compound which Nagai obtained by boiling it with alcoholic potash is β-methylumbelliferone methyl ether, as he supposed. A. R. L.

Hydrobenzoic Acid. By O. Aschan (*Ber.*, **25**, 886—888).—A criticism of some remarks by Markovnikoff (this vol., p. 714).

The author has redetermined the melting and boiling points of hydrobenzoic acid, and obtains the numbers 28° and 232—233° (corr.). Markovnikoff's numbers are 28·5—29·5° and 232—234°.

E. C. R.

Reactions of Amidobenzoic Acids. By O. de Coninck (*Compt. rend.*, **114**, 595—597 and 758—760).—When the amidobenzoic acids are heated out of contact with air with potassium, sodium, magnesium, or zinc, variable quantities of ammonia are evolved. Evolution of ammonia is also observed when these acids are heated with potassium, sodium, barium, strontium, and magnesium oxides or hydroxides, zinc oxide, &c.

Soda-lime behaves differently. If rapidly heated with the ortho-acid for a short time, carbonisation takes place, and if the residue is treated with water, a pale-violet solution is obtained. The colour is discharged by a dilute acid, but restored by a dilute alkali. Addition of dilute sodium hydroxide produces a bluish fluorescence. The meta-acid under the same conditions gives a red-brown solution; with less soda-lime, a violet solution is obtained, with a tint very different from that given by the ortho-acid. The para-acid gives no similar coloration.

When heated with copper oxide, the ortho- and para- acids give no coloration; the meta-acid yields a substance dissolving in dilute alcohol, with a pale rose colour. With barium peroxide, there is incandescence, and the meta-acid yields a garnet-red solution; the ortho- and para-acids give no soluble coloured substance. Manganese peroxide, if carefully heated with the meta-acid, yields a violet solution when the product is treated with dilute alcohol; the ortho- and para-acids yield no such coloration.

If a dilute solution of chromic acid is poured into tubes containing equal quantities of the three amidobenzoic acids, the reduction takes place immediately with the ortho-acid, more slowly with the meta-,

and still more slowly with the para-acid. Solid chromic acid, on gently heating, produces incandescence, sometimes with explosion. When heated with arsenic acid, all three amido-acids yield violet or violet-red products soluble in alcohol, but the para-acid must be heated less strongly than the other two.

Orthamidobenzoic acid dissolves in warm nitric acid, forming a garnet-red solution which rapidly becomes deep brown, but remains clear if water is added before the change of colour takes place. The meta- and para- acids give similar colorations, and the latter offers the most resistance to the action of the nitric acid. Fuming nitric acid rapidly attacks orthamidobenzoic acid in the cold, forming a deep red-brown solution which at first remains clear after dilution, but soon becomes turbid. The meta-acid is also rapidly attacked, forming a red solution which remains permanently clear after dilution. The para-acid offers greater resistance, but forms a deep red liquid; on dilution, it changes to deep yellow, and remains clear. Aqua regia dissolves the ortho-acid completely, the meta-acid less readily, the para-acid still less readily. In the first case, the colour is bright red, and there is partial precipitation on dilution, but complete dissolution on heating; in the second case, the colour is amber-yellow and afterwards red, and there is complete dissolution on adding an equal volume of water and boiling; in the third case, the colorations are the same as with the meta-acid, but dissolution after dilution is not complete.

Boiling dilute hydrochloric acid gives a pale-violet coloration with orthamidobenzoic acid, but no coloration with the meta- and para-derivatives. The meta-acid dissolves only partially in a large excess of hydrochloric acid, but the para-acid dissolves completely. Strong hydrochloric acid behaves similarly, but produces no coloration with orthamidobenzoic acid.

Boiling dilute sulphuric acid dissolves orthamidobenzoic acid, forming a pale rose-coloured solution; the meta- and para-acids give no coloration. The ortho-acid is rapidly carbonised by strong sulphuric acid, but the meta- and para-derivatives offer considerable resistance to its action. C. H. B.

Formation of Allocinnamic Acid from Phenylpropiolic Acid. By C. Liebermann and W. Scholz (*Ber.*, **25**, 950—951).—When the acid obtained by Michael and Browne by combining phenylpropiolic acid with hydrogen bromide (Abstr., 1886, 702) is boiled with zinc filings and alcohol, it yields allocinnamic acid, and perhaps also isocinnamic acid (compare Erlenmeyer, Abstr., 1891, 200). The acid reduces alkaline permanganate without the formation of benzaldehyde, and in view of this, as well as its formation from phenylpropiolic acid, the authors regard its constitution as $\begin{matrix} Br\cdot C\cdot Ph \\ \| \\ H\cdot C\cdot COOH \end{matrix}$. A. R. L.

Condensation of Cinnamic and Allocinnamic Acids. By C. Liebermann and A. Hartmann (*Ber.*, **25**, 957—961).—Cinnamic acid condenses with phenols more readily than allocinnamic acid,

thus:—At the ordinary temperature, after several months, cinnamic acid and phenols give the same phenylhydrocoumarin which is obtained at a higher temperature in a few days from allocinnamic acid (see Abstr., 1891, 1484). Hydroxyphenylhydrocoumarin, $C_{15}H_{12}O_3$, prepared from cinnamic acid and resorcinol, behaves as the corresponding product from allocinnamic acid (*loc. cit.*). An isomeric *compound*, which is insoluble in water and melts at 133°, is formed from resorcinol and allocinnamic acid; whilst a third *isomeride* is produced by dissolving quinol and cinnamic acid in glacial acetic acid (5 grams of each), adding a mixture of glacial acetic acid (2 c.c.) and concentrated sulphuric acid (7 c.c.), and heating the whole on the water-bath for three hours; it crystallises from benzene in needles, melts at 133°, is sparingly soluble in hot water, and dissolves in alkalis with a yellow colour.

Xylylphenylpropionic acid, $C_6H_3Me_2{\cdot}CHPh{\cdot}CH_2{\cdot}COOH$, is obtained when cinnamic acid (5 grams) is dissolved in metaxylene (100 grams), sulphuric acid (5 grams) slowly dropped in, and the mixture heated on the water-bath for four hours; after distilling off the excess of xylene and purifying, it forms an amorphous, resinous mass, readily soluble in hot benzene; allocinnamic acid gives the same compound. The *calcium* salt separates as a white, flocculent precipitate on adding calcium chloride to the ammoniacal solution.

Diphenylpropionic acid, $CHPh_2{\cdot}CH_2{\cdot}COOH$, is prepared by heating together allocinnamic acid, benzene, and sulphuric acid; after purification, it forms small, white needles, and melts at about 145°; the calcium salt is soluble in water, and crystallises in needles.

A. R. L.

Phenyltrimethylenecarboxylic Acids. By E. Buchner and H. Dessauer (*Ber.*, **25**, 1147—1157).—The authors have not yet succeeded in determining the constitution of the phenyltrimethylenedicarboxylic acid prepared from ethyl phenylpyrazolinedicarboxylate; they therefore propose to term it Γα1-*phenyltrimethylene*-2-3-*dicarboxylic acid*, since it yields an anhydride, and must be, therefore, either Γ cis 1-phenyl-trans-2-3-dicarboxylic acid or Γ cis 1-phenyl-cis-2-3-dicarboxylic acid. The acid is not acted on by sodium amalgam, bromine, or hydrobromic acid. The *dimethyl salt* crystallises from light petroleum in colourless needles, melts at 63°, and boils at 200—214° under a pressure of 20 mm. The *silver salt*, $C_{11}H_8O_4Ag_2$, is stable; the *hydrogen sodium salt*, $C_{11}H_9O_4Na$, crystallises from water in slender, lustrous needles. The *anhydride*, $C_{11}H_8O_3$, is formed by heating the acid in a vacuum; it melts at 134°, and was previously mistaken for the monocarboxylic acid; the original acid is regenerated by the action of soda.

Γα1-Phenyltrimethylene-2-2-3-tricarboxylic acid is obtained by the hydrolysis of the ethereal salt (see below); on the addition of light petroleum to its solution in ether, it crystallises out with $4H_2O$; the anhydrous acid melts at 188°, and is not acted on by potassium permanganate in alkaline solution. The *trimethyl salt* is prepared by heating methyl malonate (1 mol.) with sodium methoxide (2 mols.) and methyl dibromhydrocinnamate (1 mol.) in methyl alcoholic solution for eight

hours; the product is treated with water, extracted with ether, the ether removed, and the residue fractionated under reduced pressure; the compound melts at 47° and boils at 209—210° under a pressure of 20 mm.; like the acid, it is stable towards potassium permanganate in alkaline solution. The *potassium salt*, $C_{12}H_9O_6K$, crystallises from water. On heating the anhydrous carboxylic acid at 180—200° in an atmosphere of carbonic anhydride, phenylisocrotonic acid is formed; the yield is 50 per cent. of the acid employed; phenylisocrotonic acid is converted into phenyldibromobutyric acid (m. p. 136°) by the action of bromine, whilst with hydrogen bromide γ-phenylbutyrolactone and γ-phenylhydroxybutyric acid are produced. *Silver phenylisocrotonate* is unstable, and yields the acid on distillation. The calcium salt, contrary to the observations of Jayne, is sparingly soluble in water, and loses 3 mols. H_2O in a vacuum over sulphuric acid. The barium salt is also sparingly soluble, and crystallises from water in needles.

Although it is unusual for the trimethylene ring to be resolved on heating trimethylenecarboxylic acids, the formation of phenylisocrotonic acid from the acid $C_3H_2Ph(COOH)_3$ is analogous to the formation of trimethylenecarboxylic acid and butyrolactone from trimethylene-1-1-dicarboxylic acid. J. B. T.

A Correction. By E. Laves (*Ber.*, **25**, 1070—1071).—In the printing of the author's paper on trithioorthoformates certain words were omitted, so that the following correction is to be made in the abstract (this vol., p. 613, line 17 from top):—For "in presence of phenyl groups . . . . disulphones are formed"; read "the latter are oxidised directly to trisulphones, whereas the former yield disulphone sulphides in presence of phenyl groups, disulphones in presence of ethyl groups."

In the paper, "Formation of trisulphones from disulphones" (this vol., p. 614, line 2 from top), for "by the action of sodium," read "by the action of sodium and lead mercaptides and of sodium benzenesulphinate." F. S. K.

Benzenesulphonitramide. By O. Hinsberg (*Ber.*, **25**, 1092—1096).—This substance, $NO_2{\cdot}NH{\cdot}SO_2Ph$, is obtained by adding finely-powdered benzenesulphonamide (50 grams) to cooled, strong nitric acid of sp. gr. 1·48 (200 grams), then adding cooled, strong sulphuric acid (100—150 grams), and pouring the mixture into much cold water. The nitramide is extracted with ether, and recrystallised from alcohol. It forms large, transparent tables, easily soluble in water, alcohol, and ether, but precipitated in a crystalline form by the addition of mineral acids to an aqueous solution. It melts and decomposes at about 100°, nitrous oxide being evolved and benzenesulphonic acid formed. The same decomposition takes place when it is warmed with strong sulphuric acid or acetic anhydride, or is heated at 150° with hydrochloric or hydrobromic acid, or with water. Strong hydriodic acid converts it into phenyl bisulphide and ammonia; nitrous acid does not attack it; ammonium sulphide forms the ammonium salt, which is not further reduced, but stannous chloride

reduces the nitramide to benzenesulphonamide. It has an acid taste, and forms salts. The *potassium salt*, $NO_2{\cdot}NK{\cdot}SO_2Ph$, crystallises in white prisms with a slightly bitter taste. It is readily soluble in hot, very sparingly in cold, water, and is much more stable than the amide itself, not decomposing until heated to 275°. When the silver salt is treated with methyl iodide, benzenesulphomethylnitramide of known constitution, $NO_2{\cdot}NMe{\cdot}SO_2Ph$, is formed; consequently the nitramide has itself the constitution assigned above. C. F. B.

Dibenzyl Ketone and Dibenzylcarbinol. By V. Bogdanowska (*Ber.*, **25**, 1271—1277).—*Dibenzylcarbinol*, $CH(CH_2Ph)_2{\cdot}OH$, is prepared by dropping sodium in small pieces into an ethereal solution of dibenzyl ketone, cooled by water; the reaction extends over 7—8 days, and a large excess of sodium must be employed. It is a colourless, highly refractive liquid, having a sp. gr. 1·0619 at 16·5°; it boils at 327°, and gives the corresponding ketone on oxidation with potassium dichromate and dilute sulphuric acid. The *benzoyl* derivative crystallises in transparent, four-sided prisms, and melts at 50—51°. When the carbinol is reduced with hydriodic acid and phosphorus, it yields dibenzylmethane; whilst, if it is heated at 265° in a sealed tube with methyl iodide, the same hydrocarbon is obtained, but, in addition, a small quantity of another, $C_{30}H_{22}$, which melts at 268—269°.

Dihydroxydiphenyldibenzylmethane, $C(CH_2Ph)_2(C_6H_4{\cdot}OH)_2$, is obtained by fusing dibenzyl ketone with twice the calculated quantity of phenol, adding concentrated sulphuric acid, and, after 24 hours, driving the excess of phenol over with steam; the compound is obtained from the residual oil, which, after purification, solidifies and crystallises from benzene in four-sided tables.

When dibenzyl ketone is heated at 60—70° with 1 per cent. aqueous potash, a current of air being passed through meanwhile, the acid $C_{15}H_{14}O_3$, melting at 160—161°, is obtained. This acid has probably the constitution $CH_2Ph{\cdot}CPh(OH){\cdot}COOH$; it appears to give stilbene on distillation. A. R. L.

Metaphenyltoluene. By G. Perrier (*Compt. rend.*, **114**, 484—486).—An ethereal solution of metabromotoluene (1 mol.) and bromobenzene (1 mol.) is heated with sodium (excess) in a reflux apparatus at 40—50° for five hours. The product of distillation is purified from diphenyl by repeated fractionation and exposure to low temperature, and then consists of *metaphenyltoluene*, C_6H_4MePh, a liquid of aromatic odour, boiling at 270°, and not solidifying at −23°. Metaphenyltoluene is oxidised by dilute nitric acid (sp. gr. 1·14) to diphenylmetacarboxylic acid, $C_{12}H_9{\cdot}COOH$, which crystallises in nacreous plates, melts at 159°, and is identical with the acid prepared by Schmidt and Schultz from diphenylbenzene, and by Barth and Schröder from benzoic acid.

Metaditolyl, $C_6H_4Me{\cdot}C_6H_4Me$, which is obtained in small quantity as a secondary product in the above preparation of metaphenyltoluene, boils at 287—288°. It is oxidised by dilute nitric acid to metatolylbenzenemetacarboxylic acid, $C_6H_4Me{\cdot}C_6H_4{\cdot}COOH$, which crystallises

in silky needles, melts at 204°, and dissolves in alcohol, ether, and chloroform, and less freely in water. Its salts crystallise well.

Jn. W.

Dimetaditolyl. By R. Löwenherz (*Ber.*, **25**, 1032—1037; compare Täuber, Abstr., 1890, 782).—*Metanitrorthotolidine*, $C_{14}H_{15}N_3O_2$, is formed, together with a dinitro-compound, when potassium nitrate is gradually added to an ice-cold sulphuric acid solution of orthotolidine, and the salt thus produced is decomposed with alkali. It crystallises from alcohol in dark-red needles, melts at 156° with previous softening, and is insoluble in light petroleum, and only moderately easily soluble in cold alcohol and ether, but more readily in benzene and boiling glacial acetic acid. The *sulphate* crystallises in yellowish, microscopic plates, and is only very sparingly soluble in hot water, by which it is decomposed; the *hydrochloride* is a colourless, crystalline compound, and resembles the sulphate in its behaviour with hot water. By combining diazotised nitrotolidine with naphthionic acid there is formed a tetrazo-dye, corresponding with benzopurpurin 4 B, which imparts to cotton a bluish-red colour, and which has only a slightly less affinity for the cotton fibre than that of the tolidine dye, the sensibility of the two dyes as regards acids being the same. The *diacetyl* derivative, $C_{18}H_{19}N_3O_4$, crystallises from glacial acetic acid in slender, yellow needles, melts at 290°, and is soluble in hot alcohol, but only very sparingly in ether and benzene.

Dibenzylidenenitrotolidine, $C_{28}H_{22}N_3O_2$, prepared by heating an alcoholic solution of the base with benzaldehyde, crystallises from alcohol in plates, melts at 147°, and is readily soluble in benzene, but only sparingly in ether and alcohol, and insoluble in water.

Nitrodicresol, $C_{14}H_{13}NO_4$, is obtained by diazotising nitrotolidine; it crystallises from water in golden needles, melts at 187°, and is readily soluble in cold alcohol, ether, and glacial acetic acid, but more sparingly in benzene and cold water; its aqueous solution gives a reddish-orange coloration with alkalis.

Metamidorthotolidine was obtained in an impure condition by reducing the nitro-compound with tin and hydrochloric acid; it is very readily soluble in alcohol, but only very sparingly in ether and water, and resinifies on exposure to the air. The *hydrochloride* crystallises from water in prisms, and is very readily soluble in water. The *acetyl* derivative, $C_{20}H_{23}N_3O_3$, separates from alcohol in colourless crystals, does not melt below 290°, and dissolves freely in boiling alcohol, but is almost insoluble in ether and benzene.

Dimetaditolyl dicyanide, $C_{16}H_{12}N_2$, can be prepared from orthotolidine by Sandmeyer's method; it crystallises from alcohol in yellowish needles, melts at 190°, and is moderately easily soluble in ether, benzene, and glacial acetic acid, but only sparingly in light petroleum.

Ditolyldicarboxylic acid, $C_{16}H_{14}O_4$, prepared by boiling the preceding compound with moderately concentrated sulphuric acid, separates from hot, dilute alcohol as a colourless, flocculent precipitate, does not melt below 300°, and sublimes when strongly heated with partial decomposition; it is insoluble in water, and only sparingly soluble in boiling alcohol.

F. S. K.

Formation of an Orthamidoditolylamine from Parahydrazotoluene. By E. Täuber (*Ber.*, **25**, 1019—1025).—It has long been known that parahydrazotoluene under certain conditions undergoes an intramolecular change, with formation of a new substance termed paratolidine, it being assumed that the change in question was similar to that of hydrazobenzene to benzidine (*Ber.*, **3**, 554; Abstr., 1879, 239). As, however, the hydrogen atoms in the para-position to the hydrazo-group are already substituted by methyl, the amido-groups cannot occupy the para-position in the new compound as they do in benzidine, and the author, therefore, regarded it as probable that the so-called paratolidine contained the amido-groups in the peri-position, its constitution being represented by the formula $NH_2{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}NH_2$ [$(NH_2)_2 : (Me)_2 = 2 : 2' : 5 : 5'$]. The substance possessing this constitution has, however, recently been prepared by the author and Loewenherz (Abstr., 1891, 1491), and possesses very different properties from those of the so-called paratolidine, and a renewed investigation of the substance was therefore required. The results obtained showed that it is not a derivative of diphenyl but an *orthamidoditolylamine*, $C_6H_4Me{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH_2$ [NH : Me = 1 : 4 and NH : NH_2 : Me = 1 : 2 : 5] (compare Jacobsen and Fischer, this vol., p. 839, Witt and Schmidt, this vol., p. 862). It shows all the characteristic reactions of an orthodiamido-compound, giving an azimide with nitrous acid, an azonium base with benzil, and a benzenyl derivative with benzaldehyde. Schultz (Abstr., 1884, 903) obtained a ditolyl from the base by the action of nitrous acid, but the author has, under varying conditions, never observed the formation of this compound, and believes that Schultz obtained it owing to the employment of paratoluidine containing a small quantity of an isomeride.

Orthamidoditolylamine is best obtained by pouring alcohol (500 c.c.) on to parahydrazotoluene (50 grams), gradually adding a solution of stannous chloride (60 grams) in 25 per cent. hydrochloric acid (150 c.c.), cooling, and allowing the mixture to remain for 24 hours, then adding water and an excess of soda; the crude product is dissolved in hot alcohol, and the cooled solution precipitated with water. The base then forms white plates, having a fatty lustre, melts at 107°, and dissolves readily in alcohol, ether, and benzene, sparingly in light petroleum. With ferric chloride, the alcoholic solution becomes claret coloured, and the hydrochloride blood-red, whilst the colourless solution of the base in sulphuric acid becomes deep-blue on the addition of sodium nitrite, the colour gradually changing to greyish-green.

The *azonium* base, $C_{28}H_{24}N_2O$, obtained by heating orthamidoditolylamine with benzil, alcohol, and hydrochloric acid, separates from alcohol in greenish-yellow crystals melting at 173°, and readily soluble in water; when amorphous, it dissolves very easily in alcohol, ether, and benzene, but in the crystalline condition is only sparingly soluble in these liquids. The *azimide*, $\begin{matrix} N{-}N{\cdot}C_6H_4Me \\ \| \quad | \\ N{-}C_6H_3Me \end{matrix}$, forms white, granular crystals, and melts at 93°; the *benzenyl* derivative, $\begin{matrix} CPh{\cdot}N{\cdot}C_6H_4Me \\ \| \quad | \\ N{-}C_6H_3Me \end{matrix}$, obtained by heating the base with alcohol and benz-

aldehyde, crystallises from alcohol in colourless needles, and melts at 185°; the benzylidine compound is probably first formed and converted into the benzenyl base by slow oxidation. H. G. C.

Condensation of Aldehydes with Azo-compounds. By J. Barsilowsky (*Chem. Centr.*, 1892, i, 57—58; from *Bull. Acad. St. Pétersbourg* [2], **34**, 259—289).—In order to study the reaction which takes place between aldehydes and azo-compounds in the presence of dehydrating substances, the author heated benzaldehyde with azobenzene in the presence of zinc chloride, when dibenzilidenebenzidine was obtained, identical with that prepared from benzaldehyde and benzidine by Schiff. The former reaction is explained by the readiness with which azobenzene is converted into benzidine, and since the reaction takes place in the same manner in the presence of hydrochloric acid, the author concludes that the oxygen of the aldehyde group unites with the hydrogen of the amido-group. If benzaldehyde and azobenzene be heated in the absence of a dehydrating agent, no change occurs until the temperature rises to 205—210°, when the compound $O<\begin{matrix}CHPh\\|\\NPh\end{matrix}$ is obtained. It forms colourless, lustrous plates or needles, is soluble in benzene, sparingly soluble in water or mineral acids, melts at 164°, and boils at 368—370°. In a corresponding manner, the three nitrobenzaldehydes are condensed in the presence of zinc chloride, benzilidenebenzidines being formed; in the absence of a dehydrating agent, compounds corresponding with the above are obtained, in which the carbon atom and the oxygen atom of the aldehyde group and the nitrogen of the azo-group form a ring. From paranitrobenzaldehyde, in the presence of zinc chloride, there is formed *paradinitrobenzilidenebenzidine*,

$$C_{12}H_8(N{:}CH{\cdot}C_6H_4{\cdot}NO_2)_2,$$

pale-yellow plates, insoluble in water, alkalis, and light petroleum, sparingly soluble in ether and alcohol, soluble in benzene, melting point 242°; and also *paranitrobenzilidenebenzidine*, $CH(C_6H_4{\cdot}NH)_2{\cdot}C_6H_4{\cdot}NO_2$, crystallising from benzene in brown plates, melting at 221°. In the absence of zinc chloride, the compound $O<\begin{matrix}CH{\cdot}C_6H_4{\cdot}NO_2\\|\\NPh\end{matrix}$ is obtained as yellow, silky threads from benzene solution, or lustrous needles by sublimation; it melts at 210—211°. From metanitrobenzaldehyde, in the presence of zinc chloride, *dimetanitrobenzilidenebenzidine* is obtained; it forms pale yellow prisms, soluble in benzene, and melts at 237—238°. In the absence of zinc chloride, no definite result was obtained.

From orthonitrobenzaldehyde, in the presence of zinc chloride, *diorthonitrobenzilidenebenzidine* was obtained as light-yellow prisms, soluble in benzene, and melting at 221—222°. J. W. L.

Action of Paramidodimethylaniline on Ketones. By H. Vogtherr (*Ber.*, **25**, 635—640).—When paramidodimethylaniline is mixed with benzile in molecular proportion in alcoholic solution, and

a few drops of aqueous potash added, a substance of the composition $COPh{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}NMe_2$ separates out. It is deposited from alcohol in red crystals, melts at 138—139°, dissolves also in ether, and is decomposed even by traces of dilute acids into benzile and the base. A second molecule of the base could not be made to react with benzile.

Paramidodimethylaniline reacts in a similar manner with benzoylacetone. The substance formed, $C_{18}H_{20}N_2O$, crystallises from alcohol in lemon-yellow needles with a silky lustre, melts at 135—136°, dissolves also in ether, and is decomposed by dilute acids. No reaction takes place with a second molecule of the base.

When benzoïn and paramidodimethylaniline are mixed in molecular proportion in alcoholic solution, a few drops of an alkali added, and the mixture heated, the substance which separates on cooling is not a derivative of benzoïn, but a condensation product,

$$CHPh{:}N{\cdot}C_6H_4{\cdot}NMe_2,$$

of benzaldehyde with the base, and yields benzaldehyde when treated with an acid. No doubt the benzoïn had been first decomposed by the small quantity of alkali, and the base had reacted with the benzaldehyde thus formed, for it was shown that phenylhydrazine, a substance resembling amidodimethylaniline in its reactions, although it forms a condensation product with benzoïn, yet in the presence of potash yields a substance which is a condensation product of phenylhydrazine with benzaldehyde. A condensation product, $C_{22}H_{22}N_2O$, of benzoïn with amidodimethylaniline may, however, be obtained by melting together the two substances for 15 minutes in a porcelain vessel, dissolving the mass in alcohol, and boiling with animal charcoal. On cooling, orange plates separate out, which melt at 126—127°, dissolve readily in ether, and also in dilute acids without undergoing decomposition. Under other circumstances, some of the benzile derivative was formed.

The reaction of amidodimethylaniline with deoxybenzoïn is similar to that with benzoïn, and under some circumstances the benzile derivative is formed. To obtain the deoxybenzoïn condensation product, $C_{22}H_{22}N_2$, molecular proportions of the base and of deoxybenzoïn were heated for an hour at a temperature just below the boiling point of the mixture, and the mass was dissolved in alcohol and boiled with animal charcoal. On cooling, yellow needles separate, which melt at 138—139°, dissolve in ether, and are decomposed by dilute acids into deoxybenzoïn and the base.

C. F. B.

Hydroxyaurines and their Carboxylic Acids. By N. Caro (*Ber.*, **25**, 939—949).—An extension of the method of preparing certain aurine derivatives (D. R.-P., 49970; *Ber.*, **23**, Ref. 163). *Methylenedisalicylic acid*, $CH_2[C_6H_3(OH){\cdot}COOH]_2$, is obtained by the condensation of salicylic acid (2 mols.) with formaldehyde (1 mol.) in the presence of concentrated hydrochloric acid. *Aurinetricarboxylic acid*, $O{<}\begin{matrix}C_6H_3{\cdot}COOH\\ |\\ C[C_6H_3(OH){\cdot}COOH]_2,\end{matrix}$ is formed when a mixture of methylenedisalicylic acid (2 parts) and salicylic acid (1 part) is

stirred into one of concentrated sulphuric acid (13 parts) and sodium nitrite (1 part); it is poured into water, the precipitated compound dissolved in alkali and reprecipitated by hydrochloric acid; after again dissolving in alkali, sodium hydrogen sulphite is added until the solution is colourless, and it is neutralised with hydrochloric acid, when the sulphurous acid compound separates as a yellow powder; the latter, on heating at 100°, yields aurinetricarboxylic acid as a red powder having a metallic lustre, which is then crystallised from 50 per cent. alcohol. When its ammoniacal solution is boiled with lime-water, the *salt* $(C_{22}H_9O_9)_2Ca_5$ is obtained; whilst on the addition of calcium chloride to the same solution, the salt $(C_{22}H_{11}O_9)_2Ca_3$ separates. The *aluminium*, *calcium*, *barium*, and *magnesium* salts of this and all the aurinecarboxylic acids to be described are insoluble in water.

Methylenedisalicylic acid gives with β-resorcylic acid the *compound* $O<\begin{matrix}C_6H_2(OH)\cdot COOH\\ |\\ C[C_6H_3(OH)\cdot COOH]_2\end{matrix}$; with gallic acid, the *compound*

$$O<\begin{matrix}C_6H(OH)_2\cdot COOH\\ |\\ C[C_6H_3(OH)\cdot COOH]_2\end{matrix};$$

and with phenol, aurinedicarboxylic acid, $O<\begin{matrix}C_6H_4\\ |\\ C[C_6H_3(OH)\cdot COOH]_2\end{matrix}$; which, in spite of its containing one less carboxyl group, colours mordants. All these compounds form calcium salts corresponding with the number of carboxyl and hydroxyl groups present.

Methylenediresorcylic acid, $CH_2[C_6H_2(OH)_2\cdot COOH]_2$, is obtained by condensing β-resorcylic acid with formaldehyde in the presence of dilute hydrochloric acid; it separates from alcohol as a white, microcrystalline powder, melts at 236° with decomposition, and is insoluble in water. The hydroxyaurinecarboxylic acids obtained by condensing the last mentioned compound with salicylic, β-resorcylic, and gallic acids are briefly described.

Methylenedigallic acid, $CH_2[C_6H(OH)_3\cdot COOH]_2$, is formed from gallic acid and formaldehyde, and has been already prepared by Baeyer (this Journal, 1873, 501); it likewise condenses with hydroxy-acids and phenols, but the reactions must be conducted with cooling, as the products easily decompose.

Methylenediresorcinol, $CH_2[C_6H_3(OH)_2]_2$, produced from resorcinol and formaldehyde, separates from alcohol in white, microscopic crystals, and decomposes without melting at 250°.

Methylenedipyrogallol, $CH_2[C_6H_2(OH)_3]_2$, (Baeyer, *loc. cit.*), is obtained from pyrogallol and formaldehyde, and melts at 241° with decomposition. By condensing methylenediphenol (dihydroxydiphenylmethane) with phenol, aurine is obtained; whilst by condensing it with salicylic acid, aurinecarboxylic acid is produced.

The tinctorial properties of the aurinecarboxylic acids increase with the number of carboxyl groups which they contain; those derived from methylenedisalicylic acid colour alumina mordants red, and iron mordants violet; those from methylenediresorcylic acid colour alumina mordants orange-brown and iron brown; whilst

the introduction of the gallic acid residue into either produces a brownish shade. The aurinecarboxylic acids derived from methylenedisalicylic acid gave a dark line in the spectrum between D and *b*; whereas those derived from methylenediresorcylic acid exhibit, in addition to this, an absorption between *b* and F. The compound obtained from resorcylic acid and methylenedisalicylic acid belongs to the last-mentioned class; whilst aurinecarboxylic acid exhibits the absorption of the salicylic acid derivatives, and in addition to this an absorption in F. A. R. L.

Action of Hypochlorous Acid on β-Naphthaquinone. By E. Bamberger and M. Kitschelt (*Ber.*, **25**, 888—898; compare this vol., p. 494).—It was previously stated (*loc. cit.*) that an acid (m.p. 203°) is obtained when β-naphthaquinone is treated under certain conditions with hypochlorous acid. The experiments to be described show that this acid is the *δ-lactone* of *orthocarboxyphenylglyceric acid*, $C_6H_4<^{CO\text{---}O}_{CH(OH)}>CH\cdot COOH$. It is prepared by passing the chlorine from manganese dioxide (125 grams) and hydrochloric acid (1250 grams) into a solution of sodium carbonate (375 grams) in water (1250 grams), adding finely powdered β-naphthaquinone (12·5 grams) with agitation, and after five minutes acidifying with hydrochloric acid, evaporating the solution to half, and extracting it with ether. The pure compound crystallises in rhombic tables, melts at 204·5°, gives an intensive lemon-yellow colour with ferric chloride, reduces ammoniacal silver solution slowly at 100°, and when heated at 225—230° yields another acid, melting at the same temperature as that obtained by heating it with hydrochloric acid (see below), but it is not identical with it. When treated with alkali at the ordinary temperature, it behaves as a monobasic acid; whilst at 100°, salts of ortho-carboxyphenylglyceric acid, $COOH\cdot C_6H_4\cdot[CH(OH)]_2\cdot COOH$, are obtained, but these are reconverted into salts of the lactonic acid if their aqueous solutions are left for a time. When silver nitrate is added to a cold ammoniacal solution of the lactonic acid, the silver salt of the latter separates as a white precipitate soluble in boiling water; whilst at 100° the silver salt of orthocarboxyphenylglyceric acid is precipitated as a white, flocculent precipitate. The *acetyl* derivative, $C_6H_4<^{CO\text{---}O}_{CO(OAc)}>CH\cdot COOH$, crystallises in white needles, and yields a soluble silver salt crystallising in lustrous needles. When othocarboxyphenylglyceric lactone is heated with hydriodic acid and phosphorus at 160°, orthocarboxyhydrocinnamic acid (see Abstr., 1888, 712) is formed; whilst *othocarboxy-α-hydroxycinnamic lactone*, $C_6H_4<^{CO\cdot O}_{CH:C\cdot COOH}$, is produced by heating it at the same temperature with concentrated hydrochloric acid. The latter crystallises in long needles, melts at 237°, is readily soluble in hot water, sparingly in cold, does not react with acetic chloride, and reduces ammoniacal silver solution when heated with it, forming a mirror. Like the last described lactonic acid, it neutralises two equivalents of alkali at 100°,

but one only at the ordinary temperature. It is readily reduced by sodium amalgam, and is oxidised by alkaline permanganate. The above described lactonic acids have been recently obtained in a similar manner by Zincke (this vol., p. 720), who has, however, interpreted his results differently (compare also this vol., p. 859).

A. R. L.

Tetrachlororthodiketohydronaphthalene, its Hydrates and Alcoholates. By T. Zincke and T. Arnst (*Annalen*, **267**, 319—341; compare Abstr., 1188, 489).—The hydrate of tetrachlororthodiketohydronaphthalene, $C_{10}H_4Cl_4O_2,H_2O$, begins to melt at 82—83°, and at 100° the turbid liquid froths a little and becomes quite clear. The *dihydrate*, $C_{10}H_4Cl_4O_2,2H_2O$, crystallises in long, colourless needles and melts at about 90°; the trihydrate begins to melt at about 89°, the turbid liquid frothing up and becoming quite clear at 100°. The ethylate, $C_{10}H_4Cl_4O_2,EtOH + \frac{1}{2}H_2O$, crystallises unchanged from boiling light petroleum in long needles, and melts at 103—105°, with effervescence. The *methylate*, $C_{10}H_4Cl_4O_2,MeOH + \frac{1}{2}H_2O$, crystallises from light petroleum in long, colourless needles, melts at 88—89°, and decomposes over sulphuric acid.

Ethyl tetrachloro-α-hydroxyhydrindenecarboxylate,

$$CCl_2<\begin{matrix}C_6H_4\\CCl_2\end{matrix}>C(OH)\cdot COOEt,$$

is formed when the ethylate just referred to is treated with 10 per cent. sodium carbonate at the ordinary temperature. It separates from hot alcohol in colourless, transparent, seemingly monoclinic crystals, melts at 163°, and is readily soluble in ether, but only sparingly in light petroleum. The *acetyl* derivative, $C_{14}H_{12}Cl_4O_4$, separates from hot alcohol in compact crystals, melting at 119—120°. When the ethyl salt is boiled with dilute sulphuric acid, it is converted into dichloroketohydroxyhydrindenecarboxylic acid (*loc. cit.*), a crystalline compound melting at 130° with effervescence; on heating the ethyl salt with concentrated nitric acid, it is converted into *ethyl dichloroketohydroxyhydrindenecarboxylate*, $C_{12}H_{10}Cl_2O_4$, a compound which forms small, lustrous crystals, and melts at 100°.

Methyl tetrachloro-α-hydroxyhydrindenecarboxylate, $C_{11}H_8Cl_4O_3$, separates from a mixture of ether and light petroleum in colourless crystals, melts at 130—131°, and is readily soluble in methyl or ethyl alcohol; on treatment with concentrated nitric acid, it yields methyl dichloroketohydroxyhydrindenecarboxylate (m.p. 124—125°).

Tetrachloro-α-hydroxyhydrindenecarboxylic amide, $C_{10}H_7Cl_4O_2N$, is formed when anhydrous ammonia is passed into an ice-cold benzene solution of tetrachlororthodiketohydronaphthalene; it crystallises from alcohol in colourless needles, melts at 189° with decomposition, and is readily soluble in alcohol and ether, but only sparingly in benzene. The *acetyl* derivative is very unstable, and melts at about 179°. When the amide is heated with dilute sulphuric acid, it is converted into dichloroketohydroxyhydrindenecarboxylic acid, but with hot nitric acid it yields dichlorodiketohydrindene. The amide is completely decomposed by water at 120° yielding dichloroketoindene and the *amide* of dichloroketohydroxyhydrindenecarboxylic

acid; the last named compound crystallises from alcohol in colourless needles, melts at 246° with decomposition, and is only sparingly soluble in cold alcohol, and almost insoluble in ether and water.

F. S. K.

Action of Bleaching Powder and Hypochlorous Acid on Quinones. By T. Zincke (*Ber.*, **25**, 1168—1180).—The author, in conjunction with O. Scharfenberg (this vol., p. 720), has described two compounds, $C_{10}H_6O_4$ and $C_{10}H_8O_5$, obtained by the action of bleaching powder on β-naphthaquinone. The former is a dihydroxynaphthaquinone; the latter the δ-lactone of orthophenylglycerolcarboxylic acid. The author has now obtained an intermediate compound of the formula $C_{10}H_8O_4$, and believes it to be dihydroxydiketotetrahydronaphthalene.

Dihydroxydiketotetrahydronaphthalene, $C_6H_4<\begin{matrix}CO\text{——}CO\\ |\\ CH(OH)\cdot CH\cdot OH\end{matrix}$, is obtained by adding a solution of bleaching powder (110—115 c.c.) containing 3·6 per cent. of hypochlorous acid to β-naphthaquinone (10 grams) suspended in water (200 c.c.). The quinone rapidly dissolves, and the solution is then filtered and extracted with ether. On concentrating the ethereal solution, the compound is obtained pure. It crystallises in white needles, which turn red on exposure to air, melts at 95—96°, is easily soluble in alcohol, acetic acid, and hot water, more sparingly in cold water and ether, and very sparingly in light petroleum, chloroform, and benzene. When heated in the presence of mineral acids, it is partly converted into dihydroxynaphthaquinone; with bleaching-powder solution, it yields the acid $C_{10}H_8O_5$. It has remarkable reducing properties, precipitates silver from a solution of silver nitrate, and reduces ferric chloride and potassium ferricyanide. When heated in a current of hydrogen at 100—103°, 1 mol. of water is evolved and a compound is obtained which is reconverted into the dihydroxydiketone when treated with water. It is not attacked by acetic chloride in the cold, and, when heated with it, is converted into a compound which melts at 131—132°, and yields hydroxynaphthaquinone on treatment with soda. It dissolves in dilute sodium hydroxide to a colourless solution which very rapidly turns reddish-brown, and then deposits the sodium salt of hydroxynaphthaquinone. When treated with aniline in cold alcoholic solution, it yields anilido-α-naphthaquinone (m. p. 190°). When treated with aniline in acetic solution, it yields anilidonaphthaquinoneanilide (m. p. 179—180°). With toluylenediamine it yields two eurhodoles.

The *eurhodole* $C_6H_4<\begin{matrix}CO\cdot C=N\\ |\\ CH:C\cdot NH\end{matrix}>C_7H_6$ is obtained by adding the calculated quantity of toluylenediamine hydrochloride to an aqueous solution of the diketone. It crystallises from benzene in slender, white needles, melts at 183—184°, and does not form salts either with acids or with alkalis.

The *eurhodole* $C_6H_4<\begin{matrix}C(OH):C—N\\ |\quad\quad |\\ CH=\!=C—N\end{matrix}>C_7H_6$ is obtained by heating the preceding eurhodole with acetic acid or dilute hydrochloric acid.

It forms slender, yellow needles, melts at 169—170°, is easily soluble in alcohol and benzene, and forms salts both with acids and with alkalis.

The *oxime*, $C_6H_4<\begin{matrix}CO\cdot C{:}N\cdot OH\\ CH{:}C\cdot OH\end{matrix}$ or $C_6H_4<\begin{matrix}CO--C{:}N\cdot OH\\ C(OH){:}CH\end{matrix}$, is obtained by adding excess of an aqueous solution of hydroxylamine hydrochloride to a concentrated, alcoholic solution of the diketone. It crystallises in slender, lustrous, yellow needles, is easily soluble in alcohol and ether, sparingly so in benzene and light petroleum, melts about 152—155° with a violent explosion, and is decomposed by boiling water and by cold, aqueous soda. E. C. R.

Action of α- and β-Naphthylamine on Ethyl Bromosuccinate. By C. Hell and R. Poliakoff (*Ber.*, **25**, 965—972).—When ethyl bromosuccinate and α-naphthylamine are mixed together in the proportion of 1 mol. of the former to rather more than 2 mols. of the latter, and the mixture heated to 100°, a reaction quickly takes place with separation of a solid substance. The latter, after removal of the liquid portion and washing with ether, consists of α-naphthylamine hydrochloride, mixed with a greenish-grey powder, the quantity of which increases when a larger proportion of naphthylamine is employed, or when the heating is continued for a longer time. The oily product solidifies after a time, and on recrystallisation from alcohol forms stellate groups of needles melting at 150°, which are insoluble in water, sparingly soluble in ether and light petroleum, more readily in chloroform. It consists of *ethyl α-naphthylamidosuccinate*, $COOEt\cdot CH(NH\cdot C_{10}H_7)\cdot CH_2\cdot COOEt$, and dissolves in concentrated acids, but is reprecipitated by water. When heated with an excess of alcoholic potash, it is decomposed, but, with the theoretical quantity at 40—50°, it yields the corresponding potassium salt as a voluminous crystalline powder, which, on treatment with acids, yields free *α-naphthylamidosuccinic acid* or *α-naphthylaspartic acid*, $COOH\cdot CH(NH\cdot C_{10}H_7)CH_2\cdot COOH$. This forms a white, crystalline powder, which melts at 210° with decomposition, and dissolves readily in alcohol and chloroform, but only sparingly in water and benzene; *barium* and *calcium* salts form white, crystalline powders.

When the ethyl salt is treated with α-naphthylamine, or when a large excess of the latter is heated with ethyl bromosuccinate, considerable quantities of the *dinaphthylamide* of *α-naphthylamidosuccinic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot CH(NH\cdot C_{10}H_7)CH_2\cdot CO\cdot NH\cdot C_{10}H_7$, are formed, together with the green substance previously mentioned, which consists of the compound $COOEt\cdot CH(NH\cdot C_{10}H_7)CH_2\cdot CO\cdot NH\cdot C_{10}H_7$.

The former is separated by treatment with cold alcohol, and crystallises in silvery needles or plates which melt at 276—277° with decomposition. The second compound may be obtained pure by recrystallisation from boiling absolute alcohol, but retains its green colour; it melts at 223° with decomposition.

β-Naphthylamine reacts in a similar manner with ethyl bromosuccinate; the *ethyl β-naphthylamidosuccinate* forms an oil which boils with slight decomposition at 108° under a pressure of 20 mm. When carefully hydrolysed, it yields the corresponding *β-naphthylamidosuc-*

cinic acid, which is much less stable than the α-acid, and becomes brown in the air, especially in presence of acids and alkalis; it melts with decomposition at 189°. By the further action of β-naphthylamine the *ethyl mononaphthylamide* and the *dinaphthylamide* are obtained; the former is a yellow, microcrystalline powder which melts at 215° with decomposition; the latter forms golden plates, and melts at 250° with decomposition. H. G. C.

Homonucleal Amidonaphthols and Related Derivatives. By E. Grandmougin and O. Michel (*Ber.*, **25**, 972—985).—In consequence of the recent communications of Heermann (Abstr., 1891, 1379) and Seidel (this vol., p. 721) on the above subject, the authors publish the results they have obtained in the same field, although these are not yet completed.

1 : 2-Nitronaphthol, $OH\cdot C_{10}H_6\cdot NO_2$ [OH : NO_2 = 1 : 2], is best prepared by oxidising finely-divided 1 : 2-nitrosonaphthol with nitric acid according to the method of Stenhouse and Groves (this Journal, 1877, ii, 51); the product is distilled in a current of steam, 1 : 2-nitronaphthol passing over in a state of purity. Its *silver* salt, $C_{10}H_6NO_3\cdot Ag$, forms a voluminous, red precipitate, and its *acetyl* derivative $OAc\cdot C_{10}H_6\cdot NO_2$ large, pale-yellow needles, which yield salts of the nitronaphthol on treatment with alkalis.

1 : 2-*Amidonaphthol*, $OH\cdot C_{10}H_6\cdot NH_2$, is formed by the reduction of 1 : 2-nitronaphthol and of orthohydroxyazo-derivatives of α-naphthol, but is best prepared according to the method of Liebermann and Jacobsen (Abstr., 1882, 521) by reducing 1 : 2-nitrosonaphthol with stannous chloride and hydrochloric acid, removing the tin by hydrogen sulphide, evaporating, and filtering from oxidation products. The hydrochloride separates out on cooling, and is purified by dissolving in boiling water, and reprecipitating with concentrated hydrochloric acid, a little sulphurous acid being also added. The impure salt quickly undergoes decomposition, and does not react smoothly with reagents; on acetylation, it yields a mixture of different products. The ethers of 1 : 2-amidonaphthol may be obtained by the method of Heermann (*loc. cit.*), or by the reduction of the ethers of orthohydroxyazo-compounds of α-naphthol; they are well crystallised substances, are volatile with steam, and yield diazo-compounds which combine with alkaline phenol solutions, forming beautiful, red colouring matters.

1 : 4-Amidonaphthol was prepared by the method already described by Seidel (*loc. cit.*), the stannous chloride being obtained by dissolving the requisite quantity of tin in hydrochloric acid, which avoids the difficulties often experienced owing to the employment of oxidised or adulterated tin salts. The crude hydrochloride is purified in the same manner as the hydrochloride of the 1 : 2-compound. Unlike the latter, 1 : 4-amidonaphthol yields well crystallised derivatives, the reactions proceeding very smoothly; nitrous acid gives, however, no trace of a diazo-compound, but converts it at once into α-naphthaquinone with evolution of nitrogen, the yield of the quinone being very satisfactory; 1 : 4-diamidonaphthalene is acted on by nitrous acid in the same manner, no diazo-derivatives being formed. *Diacetyl-*

1 : 4-*amidonaphthol*, $OAc{\cdot}C_{10}H_6{\cdot}NHAc$, is the sole product of the action of acetic anhydride and sodium acetate on 1 : 4-amidonaphthol hydrochloride; it forms white, prismatic crystals, melts at 158°, sublimes even at 110°, and is insoluble in alkalis.

1 : 4-Nitronaphthol ethyl ether was prepared by the authors in the manner which has also been recently described by Heermann, whose description they confirm. On reduction, it yields the corresponding 1 : 4-*amidonaphthol ethyl ether* $OEt{\cdot}C_{10}H_6{\cdot}NH_2$, the hydrochloride of which forms well-developed crystals. The same compound may be also obtained by the reduction of paraphenylazo-α-naphthol ethyl ether, which is interesting as showing that in these ethers the ethyl group is combined with the oxygen (compare Goldschmidt and Brubacher, Abstr., 1891, 1209). The amido-compound readily yields diazo-derivatives, which combine with phenols to form reddish-violet colouring matters.

2 : 1-Amidonaphthol is most readily prepared by the reduction of Orange II (β-naphtholazobenzeneparasulphonic acid) with stannous chloride and hydrochloric acid. The hydrochloride separates in an almost pure condition on cooling in the form of lustrous, white crystals which rapidly become violet; they may be further purified by precipitation from aqueous solution with concentrated hydrochloric acid. On oxidation, this compound, as is well known, yields β-naphthaquinone, which is most readily prepared in this manner, the freshly prepared amidonaphthol hydrochloride (which need not be dried) being mixed with dilute sulphuric acid and poured into a solution of potassium dichromate; the β-naphthaquinone separates out in a pure condition, and is filtered off and dried at the ordinary temperature. 200 grams of Orange II yield 55 grams of β-naphthaquinone, or 60 per cent. of the theoretical quantity. The filtrate contains considerable quantities of phthalic acid.

Nitrous acid also converts 2 : 1-amidonaphthol into β-naphthaquinone without formation of an intermediate diazo-compound; with acetic anhydride and sodium acetate, it yields a mixture of acetyl derivatives, the *diacetyl* derivative being the chief product; smaller quantities of the acetylamido-β-naphthol $OH{\cdot}C_{10}H_6{\cdot}NHAc$, described by Böttcher (Abstr., 1883, 1113), are also obtained. H. G. C.

Products of the Reduction of Alkylated Azo-Colours of the Naphthalene Series. By O. N. Witt and C. Schmidt (*Ber.*, **25**, 1013—1019).—The methyl and ethyl ethers of anilineazo-α-naphthol may be readily prepared according to the method described by Zincke and Bindewald (Abstr., 1885, 391); in addition to the properties there mentioned, these ethers are distinguished by the fact that they dissolve in sulphuric acid or alcoholic hydrochloric acid with a reddish-violet coloration, which changes in a short time to deep-blue, owing to the elimination of the alkyl group and formation of the phenol.

When the ethyl ether is treated with stannous chloride and hydrochloric acid in presence of alcohol, it is not converted into aniline and ethoxy-α-naphthylamine, but yields a mixture of two bases, which can be separated by fractional crystallisation of the hydro-

chlorides. The base which yields the more easily soluble hydrochloride will be described in a later communication. The less soluble hydrochloride, on treatment with ammonia, yields the free base, which crystallises from alcohol in snow-white, nacreous plates, melts at 167°, and shows a greyish-green fluorescence in dilute alcoholic solution. It has the composition $C_{18}H_{18}N_2O$, and the authors at first believed that the hydrazo-compound had been formed, and had then undergone the intramolecular change corresponding to the formation of benzidine from hydrazobenzene, in which case it would be an ethoxydiamidophenylnaphthalene,

$$OEt\cdot C_{10}H_5(NH_2)\cdot C_6H_4\cdot NH_2 \ [OEt : C_6H_4\cdot NH_2 : NH_2 = 1 : 3 : 4].$$

The behaviour of the base towards oxidising agents, however, renders this view impossible, for nitric acid converts it into the bright-red compound, α-naphthaquinoneanilide, $C_{10}H_5O_2\cdot NHPh$ [O : O : NHPh = 1 : 4 : 3], and nitrous acid yields a mixture of the same compound with a colourless, crystalline substance, having the composition $C_{18}H_{15}N_3O$. The formation of the first-named derivative is most easily explained by supposing that, instead of the benzidine intramolecular change, the hydrazo-compound first formed is converted into an amidophenylnaphthylamine derivative, namely, *ethoxyphenyl-orthodiamidonaphthalene*, $OEt\cdot C_{10}H_5(NH_2)\cdot NHPh$ [OEt : NH_2 : NHPh = 1 : 4 : 3] (compare Jacobsen and Fischer, this vol., p. 839; Täuber, this vol., p. 853). This also explains the formation of the compound $C_{18}H_{15}N_3O$, which would be the azimide, $OEt\cdot C_{10}H_5<^{NPh}_{\ \ N}\!\!>N$; it crystallises in vitreous rhombohedra or needles, and melts at 160°. In order to further characterise it as an orthodiamido-derivative, it was boiled with formic acid, and thus converted into the *methenyl* derivative, $OEt\cdot C_{10}H_5<^{NPh}_{\ \ N}\!\!>CH$, which crystallises in needles melting at 184—186°. Further it unites with benzile in presence of acetic acid, forming *ethoxyphenylnaphthostilbazonium hydroxide*, the *chloride* of which, $OEt\cdot C_{10}H_5<^{NPhCl\cdot CPh}_{N\text{——}C\,Ph}$, crystallises in glistening yellow needles, fairly soluble in water and readily in alcohol, forming pure yellow solutions; these show a remarkable, luminous green fluorescence. The *nitrate* is very sparingly soluble, and the free *hydroxide* forms pale-yellow crystals.

Paratoluidineazo-α-naphthol may be converted into the methyl and ethyl ethers by the action of alcoholic potash and methyl iodide or ethyl bromide. The *methyl* ether forms red prisms, melting at 100—101°, and the *ethyl* ether melts at 125°. The yield of these compounds is not nearly so good as with the ethers of aniline-azo-α-naphthol; but on reduction they only yield a single base, and not a mixture of two bases, as is the case with the derivatives of the latter compound. H. G. C.

Oxidation of Acenaphthene. By C. Graebe and E. Gfeller (*Ber.*, **25**, 652—657).—A description is given of the details by observing which an almost theoretical yield of naphthalic acid may

be obtained when acenaphthene is oxidised with potassium dichromate and acetic acid.

After this acid has been removed from the product of the reaction by digesting with 5 per cent. aqueous soda, *acenaphthenequinone*, $C_{10}H_6<\begin{matrix}CO\\CO\end{matrix}>$ [CO : CO = 1 : 1'], may be extracted with a hot solution of sodium hydrogen sulphite, and precipitated from this solution by the addition of acids. It crystallises and sublimes in fine, yellow needles, melts at 261°, and dissolves in benzene and acetic acid. When it is boiled with 30 per cent. aqueous potash, and a mineral acid added to the solution, a monobasic acid, $C_{12}H_8O_3$, is precipitated, which, unlike naphthalic acid, dissolves in carbonates in the cold, even after being heated to its melting point. It melts at 172°, crystallises from alcohol in needles, is converted by oxidation into naphthalic acid, and forms characteristic compounds with phenylhydrazine and hydroxylamine. It is therefore probably either

$$CHO\cdot C_{10}H_6\cdot COOH \quad \text{or} \quad C_{10}H_6<\begin{matrix}CH(OH)\\CO\text{——}\end{matrix}>O.$$

Naphthalaldehydic acid. Oxynaphthalide.

It yields a *monacetyl derivative* when heated with acetic anhydride at 180°. That acenaphthenequinone reacts with potash in a different manner from phenanthraquinone, &c., is explained from stereochemical considerations.

A *diketone*, probably $C_{10}H_6<\begin{matrix}CO\ CO\\|\quad\ |\\C\text{—}C\end{matrix}>C_{10}H_6$, is obtained by crystallising from chloroform the residue left after extraction with sodium hydrogen sulphite. It forms orange needles which melt at 294°, and after sublimation resemble alizarin. It dissolves but sparingly in benzene and acetic acid, takes up two atoms of bromine, yields a derivative $C_{24}H_{12}O{:}N_2HPh$, with phenylhydrazine, and is oxidised by dichromate and acetic acid to naphthalic acid. C. F. B.

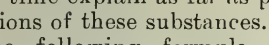
Preparation of β-Alizarinamide. By C. Lauth (*Bull. Soc. Chim.* [3], **6**, 836).—Nitroalizarin (1 part) is dissolved in dimethylaniline (4 parts), to which either syrupy dimethylaniline chloride (1 part) or hydrochloric acid (0·75 part) is added, and the mixture is heated gradually to 150°, until the product dissolves with a pure blue colour in aqueous soda. The product, after treatment with hot dilute hydrochloric acid to remove excess of dimethylaniline, is dissolved in hot dilute sodium hydroxide solution, leaving a slight residue of a brown oxidation product of dimethylaniline, and the amidoalizarin is precipitated from the alkaline solution by hydrochloric acid. Nitroalizarin is reduced more slowly when similarly treated either with aniline or dimethylaniline in presence of sulphuric acid.

T. G. N.

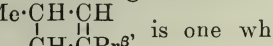
Constitution of Turpentine and Camphor. By J. N. Collie (*Ber.*, **25**, 1108—1118).—In this paper an attempt is made to suggest formulæ for turpentine, camphor, and camphoric acid, which shall show the connection of these compounds with one another, and at the

same time explain as far as possible the known reactions and decompositions of these substances.

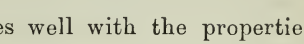
The following formula suggested for turpentine (pinene):—



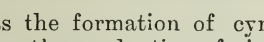
is one which agrees well with the properties of that substance; such as the formation of cymene from pinylamine and pinyl dichloride, also the production of pinol, terpenylic acid, and terebic acid by oxidation. It contains a 6-carbon ring, but yet should behave also as an ethylenic hydrocarbon; at the same time it is capable of showing the conversion of pinene into camphor and camphoric acid.



Pinene.



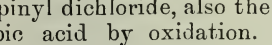
Pinene hydrochloride.



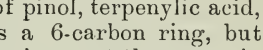
Camphene.

This formula differs from that proposed by Wallach in that it contains *no ethylenic bond*. This is in agreement with the optical and other physical properties of camphene.

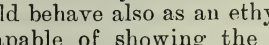
The conversion into camphor is explained as follows:—



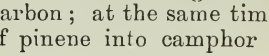
Camphene.



Camphene hydrochloride.



Intermediate product.

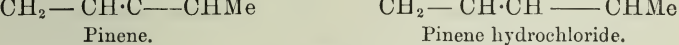


Borneol.

Camphor.

This formula accounts for the formation of such substances as paracymene, metacymene, dimethylethylbenzene, carvacrol, orthocresol, &c., from camphor.

During the oxidation of camphor to camphoric acid a considerable change in the molecule is assumed to take place in order to harmonise with the idea that camphoric acid is a hexamethylene derivative.



Camphor



Camphoric acid.

By using exactly the same molecular rearrangement as that employed above, the author shows how camphoic acid (by oxidation of camphene), cineolic acid (by the oxidation of cineol), and campholic acid (from camphor), may all possibly be hexamethylene derivatives. J. N. C.

Menthol. By A. Berkenheim (*Ber.*, **25**, 686—698).—When menthol, $C_{10}H_{19}OH$, is added in successive small portions to a carefully cooled mixture of phosphoric chloride and light petroleum, there is formed from 100 grams of menthol (1) 70 grams of *menthyl chloride*, $C_{10}H_{19}Cl$, an optically inactive liquid boiling at 209·5—210·5° (uncorr.), and having the sp. gr. at 0°/0° = 0·9565 and at 15°/15° = 0·947, and (2) 15 grams of a menthene, $C_{10}H_{18}$, boiling at 167—169° (uncorr.). This menthene, when warmed with phosphoric chloride, yields a *chloride*, $C_{10}H_{17}Cl$, boiling at 204—208°. Menthyl chloride is not affected by zinc and hydrochloric acid, and is converted by zinc-dust and acetic acid into the above-mentioned menthene; but it is reduced when heated for 30 hours at 200° with hydriodic acid and phosphorus in a sealed tube. *Menthonaphthene*, $C_{10}H_{20}$, boiling at 169—170·5°, is thus obtained. It is an inactive liquid, possessing only a feeble odour when pure, and the sp. gr. at 0°/0° = 0·8067 and at 15°/15° = 0·796. It does not take up bromine, is not attacked by strong sulphuric or nitric acid at the ordinary temperature, gives when heated with fuming nitric acid a liquid nitro-derivative, and with bromine and aluminium bromide a viscid bromide. If the heating in the sealed tube is continued for only 15—20 hours, some *menthyl iodide*, $C_{10}H_{19}I$, is also obtained; this, when not quite pure, boils at 140—143° under 30 mm. pressure, and has a sp. gr. at 15°/15° = 1·357. When chlorine is allowed to react with the vapours of menthonaphthene, an inactive liquid is obtained, volatile with steam, boiling at 208—210°, and with a sp. gr. at 0°/0° = 0·9553. It would seem to be identical with the above-mentioned menthyl chloride. When menthyl chloride (70 grams) is heated with potassium acetate and acetic acid for 20 hours in a sealed tube at 150°, some (20 grams) is left unaltered, and some menthene, $C_{10}H_{18}$ (25 grams), is formed. This menthene boils at 170—171°, has sp. gr. at 0°/0° = 0·8287 and at 20°/20° = 0·816, and refractive index $[n]_D$ = 0·145359 at 20°, corresponding with a molecular refraction of 45·06 (theory for one double bond = 45·65, for two 47·34). It oxidises readily in the air. But whilst the menthene obtained from menthol is dextrorotatory with a maximum rotation of +20°, this menthene, obtained from inactive menthyl chloride, is lævorotatory (in a thickness of 200 mm. $[\alpha]_D$ = −56°), and the menthyl chloride which, as mentioned above, was not converted into menthene, is found to be no longer inactive, but is now lævorotatory (in a thickness of 200 mm. $[\alpha]_D$ = −62°). The inactive menthyl chloride must thus have consisted of a mixture of dextro- and lævo-rotatory varieties, and the former was converted into lævorotatory menthene, while the latter was unattacked. By further heating with potassium acetate and acetic acid, it may, however, be converted into a dextrorotatory menthene boiling at 167—169°; in a thickness of 50 mm. $[\alpha]_D$ = +28°.

Menthone, $C_{10}H_{18}O$, was prepared by the action of chromic acid on menthol in acetic acid solution, and warmed with phosphoric anhydride. A diterpene, $C_{20}H_{32}$, was obtained, together with a hydrocarbon $C_{10}H_{18}$ which was not isolated. The diterpene is a very viscid, fluorescent, inactive liquid boiling at 320—325°; it takes up bromine and hydrochloric acid, and yields a yellowish, amorphous nitro-product when treated with fuming nitric acid. When menthone is added in successive small portions to a cooled mixture of phosphoric chloride and light petroleum, a *monochloride*, $C_{10}H_{17}Cl$, and a *dichloride*, $C_{10}H_{18}Cl_2$, are obtained. The monochloride boils at 205—208°, has the sp. gr. at 0°/0° = 0·9833 and at 15°/15° = 0·970, and is lævorotatory; in a thickness of 50 mm. $[\alpha]_D = +30°$, of 75 mm. $[\alpha]_D = +45°$. The dichloride boils at 150—155° under 60 mm. pressure, and has the sp. gr. at 0°/0° = 1·0824. The monochloride is doubtless formed from the dichloride by the loss of a molecule of hydrochloric acid, but it was not found possible to remove the second molecule from the monochloride. When bromine is added to a cooled acetic acid solution of menthene, *menthene dibromide*, $C_{10}H_{18}Br_2$, is formed. It is a rather viscid oil, boiling at 167—172° under 50 mm. pressure, and with the sp. gr. at 0°/0° = 1·4453. When it is heated with alcoholic potash for 15 hours on the water-bath, a hydrocarbon $C_{10}H_{16}$ is obtained. This boils at 172—174° (uncorr.), has an odour like that of limonene, and the sp. gr. at 0°/0° = 0·8540 and at 20°/20° = 0·8408; it unites with bromine and hydrochloric acid.

Terpine hydrate, $C_{10}H_{20}O_2 + H_2O$, was heated for 20 hours with strong hydriodic acid on the water-bath. The products were an *iodide*, $C_{10}H_{19}I$, a *diterpene*, $C_{20}H_{32}$, and possibly a hydrocarbon, $C_{10}H_{18}$, boiling at 167—170°. The diterpene boils at 320—325°, has the sp. gr. at 0°/0° = 0·9521 and at 20°/20° = 0·9428, and resembles very closely in its properties and reactions the diterpene obtained from menthone. The iodide is an oil with an odour like that of the naphthene iodides; it boils at 138—142° under 30 mm. presssure, and has the sp. gr. at 15°/15° = 1·370. When it is treated with silver acetate, ether added, and the whole allowed to remain for two days, an acetate is obtained, and a hydrocarbon, $C_{10}H_{18}$, boiling at 168—170°. This latter has at 21° sp. gr. = 0·813 and refractive index $[n]_D = 1·45339$, corresponding to a molecular refraction of 45·89 (theory for one double bond 45·64). The acetate was hydrolysed by warming it with the theoretical amount of alcoholic potash on the water-bath. The alcohol, $C_{10}H_{20}O$, thus obtained boils at 210—214°, and has an odour like that of menthol, but it cannot be got to solidify. It is inactive, and has the sp. gr. at 0°/0° = 0·9151 and at 15°/15° = 0·9063.

Menthol has thus been shown to be connected with the naphthenes; the particular naphthene obtained from it must have a ring of 6 carbon atoms, since menthol can be converted into cymene. It is also connected with the terpenes, for terpine hydrate yields an alcohol, $C_{10}H_{20}O$, much resembling menthol; and, further, from menthol has been obtained a hydrocarbon, $C_{10}H_{16}$, which possesses the properties of a terpene. C. F. B.

Oxygen Compounds of Ethereal Oils. By F. W. Semmler and F. Tiemann (*Ber.*, **25**, 1180—1188).—The authors have come to the conclusion that the characteristic odour of many ethereal oils is not entirely dependent on the terpene or camphor-like constituents which they contain; but that alcohols, ethereal salts, aldehydes, and ketones of the aliphatic series essentially influence the odour. They have accordingly commenced a research on these aliphatic compounds.

Oil of bergamot is composed of the following constituents :—Limonene, 40 per cent.; dipentene, 10 per cent.; linaloöl, 25 per cent.; linaloöl acetate, 20 per cent.; and bergaptene, 5 per cent. A preparation, which smells exactly like oil of bergamot, cannot be obtained by mixing the above compounds, as the odour of the oil is influenced by the very slight quantity of other compounds which it contains. Oil of bergamot yields a small quantity of a crystalline compound when treated with sodium hydrogen sulphite. It cannot be distilled at the ordinary pressure, but under 15 mm. boils without decomposition until the bergaptene begins to distils over. At 60—65°, almost pure limonene comes over; at 77—82°, dipentene; at 87—91°, linaloöl (Abstr., 1891, 539); and at 99—105°, linaloöl acetate.

Linaloöl acetate, $C_{10}H_{17}\cdot OAc$, has a sp. gr. 0·8951 at 20°/20°, is lævorotatory, and has the characteristic odour of oil of bergamot. It is easily hydrolysed with alcoholic potash, and the linaloöl may be extracted from the mixture with ether. Linaloöl so obtained boils at 88—90° under 15 mm., and has a sp. gr. 0·8724 at 20°/20°.

"Oil of petitgrain" has a sp. gr. 0·8891 at 20°/20°, and consists of aurantiol acetate (about 70 per cent.), limonene, a high boiling sesquiterpene, and oxygenated compounds, which have a considerable influence on the odour. *Aurantiol acetate*, $C_{10}H_{17}\cdot OAc$, boils at 102—106° under 15 mm. pressure, and has a characteristic, pleasant odour, and sp. gr. 0·8988 at 20°/20°. *Aurantiol*, $C_{10}H_{18}O$, is obtained by heating the acetate with alcoholic potash, boils at 93—95° under 15 mm., has a sp. gr. 0·8691 at 20°/20°, directly adds on 4 atoms of bromine, and is lævorotatory; $n_d = 1·4682$.

Oil of lavender is lævorotatory, cannot be distilled at the ordinary pressure, and consists of lavendol, lavendol acetate, a small quantity of limonene, a sesquiterpene, and oxygenated compounds which greatly influence the odour. *Lavendol*, $C_{10}H_{18}O$, is the chief constituent of the oil, boils at 85—91° under 15 mm. pressure, has a sp. gr. 0·8672 at 20°/20°, is lævorotatory, and has a characteristic odour; $n_d = 1·4651$. *Lavendol acetate* forms about 10 per cent. of the oil, boils at 97—105° under 15 mm., has a sp. gr. 0·8972 at 20°/20°, and is lævorotatory. E. C. R.

Camphene and Camphoric Acid. By W. O. Wallach (*Ber.*, **25**, 916—927).—The author's experiments, and those of Wagner, have shown, in opposition to those of Brühl, that camphene is an unsaturated compound. Brühl, however (this vol., p. 625), has acknowledged the inaccuracy of his conclusions, but has raised several objections to the author's method of preparing camphene by heating bornyl chloride with aniline; the author points out, however,

that the conditions published by him were not obeyed. The melting point of camphene given by Brühl (53—54°) is too high, that previously given by the author (49°) being established.

Brühl (this vol., p. 203) puts forward tetramethylene formulæ for camphor and camphoric acid; the author states that he can find nothing in Brühl's experiments which serves for the discussion of the constitution of the compounds in question. Brühl considers that camphoric acid is an unsaturated compound, but such a view is untenable in the light of Bamberger's experiments, and the work of v. Baeyer on unsaturated acids generally. Whilst the arguments employed by Brühl can be used in support of other formulæ, there are several objections to the tetramethylene formulæ, which are not mentioned by him. Wreden has shown (this Journal, 1877, ii, 446) that two hydrocarbons, C_8H_{16} and C_8H_{14}, which he believed to be hexahydro- and tetrahydro-metaxylene, are formed by reducing camphoric acid, whereas, if it possessed a tetramethylene formula, it ought to furnish an unsaturated hydrocarbon, C_8H_{14}. The author has repeated Wreden's experiments, and isolated a saturated hydrocarbon giving numbers on analysis agreeing with the formula C_8H_{16}; it also agreed with Wreden's description of his compound, and, like the latter, yielded trinitrometaxylene (m. p. 180°) on nitration. The presence of a hydrocarbon containing less hydrogen could not, however, be decided. The author points out in conclusion that Brühl's first communications on the terpenes contained only physical experiments, and without depreciating the value of these, he considers that too much stress has been laid on them. A. R. L.

Derivatives of Santonin. By P. Gucci and G. Grassi-Cristaldi (*Gazzetta*, **22**, i, 1—55).—*Santoninamine*,

$$\begin{array}{c} NH_2\cdot CH\cdot CMe:C\cdot CH_2\cdot CH_2\cdot CH\text{—}CHMe. \\ \quad\quad\quad\

readily in water. It is very unstable, changing, even during crystallisation, to a yellow, insoluble compound. The *hydrochloride* obtained from the freshly prepared base crystallises from alcohol in monoclinic prisms, $a : b : c = 0{\cdot}6206 : 1 : 0{\cdot}2418$; $\beta = 82° 52' 30''$, melts at 199°, and dissolves readily in water. On heating the aqueous solution to 100°, it decomposes, hyposantonin being formed. It is lævogyrate, $[\alpha]_D = -136{\cdot}83$. The *platinochloride*,

$$(C_{15}H_{21}NO_2)_2,H_2PtCl_6,$$

forms tabular or acicular, orange-red crystals, or occurs in the amorphous condition.

On heating santoninamine or one of its salts with nitrous acid, hyposantonin is formed, with evolution of nitrogen. The reaction may be represented by the equation $C_{15}H_{21}NO_2 + HNO_2 = N_2 + 2H_2O + C_{15}H_{18}O_2$, but a compound $C_{15}H_{20}O_3$, containing 1 mol. H_2O more than hyposantonin, is probably formed as an intermediate product. In aqueous solutions, santoninamine remains unaltered in the cold, but, on warming, it is entirely split up into hyposantonin and ammonia. Aqueous solutions of its salts are likewise stable in the cold, but begin to decompose at 60°

Hyposantonin, $\begin{matrix} CH\cdot CMe{:}C\cdot CH_2\cdot CH_2\cdot CH\text{—}CHMe \\ CH\cdot CMe{:}C\text{———}CH\cdot O\cdot CO \end{matrix}$, has already been described (Abstr., 1890, 904); it melts at 152—153°, and crystallises in rhombic tables, $a : b : c = 0{\cdot}718 : 1 : 1{\cdot}36$. It is dextrorotatory, $[\alpha]_D = +32{\cdot}37$ to $+32{\cdot}71$. In alkaline solutions, hyposantonin changes slowly in the cold, and rapidly on heating into hyposantonic acid, of which it appears to be the lactone.

Hyposantonic acid, $\begin{matrix} CH\cdot CMe{:}C\cdot CH_2\cdot CH_2\cdot CH\cdot CHMe\cdot COOH \\ CH\cdot CMe{:}C\text{———}CH\cdot OH \end{matrix}$, is best prepared by pouring a boiling alcoholic solution of hyposantonin into boiling baryta-water, and decomposing the cold, dilute solution of the barium salt with a slight excess of extremely dilute hydrochloric acid. When pure, the acid crystallises in large, transparent, monoclinic tables, $a : b : c = 1{\cdot}421 : 1 : 0{\cdot}954$; $\beta = 81° 47'$. It is freely soluble in strong alcohol, moderately so in ether, but only very sparingly in cold benzene or chloroform. The crystals phosphoresce with an intense green light when crushed. On treatment with acetic anhydride, the acid loses 1 mol. H_2O, and is quantitatively converted into hyposantonin. On heating the acid alone to 100°, it likewise loses 1 mol. H_2O, but the product is isohyposantonin. It is lævogyrate, $[\alpha]_D = -4{\cdot}62$.

Isohyposantonin, previously described (Abstr., 1890, 902—904), melts at 167·5—168·5, and crystallises in rhombic pyramids, $a : b : c = 0{\cdot}9127 : 1 : 1{\cdot}8148$. It is lævorotatory, $[\alpha]_D = -73{\cdot}73$.

Isohyposantonic acid, $C_{15}H_{20}O_3$, is prepared by pouring a boiling alcoholic solution of isohyposantonin into baryta-water and decomposing the barium salt with dilute hydrochloric acid. It is very unstable, and cannot be crystallised from any solvent on account of its ready conversion into isohyposantonin. Unlike the latter, it dissolves in cold, concentrated alcohol, and the solution is only slowly

decomposed. It is dextrorotatory, $[\alpha]_D = +71{\cdot}56$. The *silver* salt, $C_{15}H_{19}O_3Ag$, was also prepared. On treatment with methyl iodide, the silver salts of both hypo- and isohypo-santonic acid yield iso-hyposantonin.

Dihydrosantinic (dihydrodimethylnaphthylpropionic) acid,

$$\begin{array}{l} CH{\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH_2 \\ \| \quad\quad\quad\quad\quad\quad | \\ CH{\cdot}CMe{:}C{\cdot}CH{:}C{\cdot}CHMe{\cdot}COOH' \end{array}$$

and *dihydroisosantinic* acid are best prepared together by passing a current of hydrogen chloride through a solution of hyposantonin or isohyposantonin in 90 per cent. alcohol, distilling at a reduced pressure, neutralising the product with sodium carbonate, extracting with ether, and distilling. The acids are obtained pure from their barium salts, and separated by fractional crystallisation from 90 per cent. alcohol. These acids are isomeric with each other, and with the lactones from which they are prepared, all having the percentage composition corresponding with the formula $C_{15}H_{18}O_2$. Dihydrosantinic acid forms a white, crystalline powder, melts at 120—121°, and dissolves readily in cold alcohol, ether, chloroform, and benzene, but is insoluble in water. It is dextrorotatory, $[\alpha]_D = +62{\cdot}07$ to $69{\cdot}69$. Dihydroisosantinic acid is also obtained as a finely crystalline powder, melts at 96—97°, dissolves in alcohol, &c., more freely than the preceding acid, but is insoluble in water. It is inactive to light.

On treating dihydrosantinic acid with bromine in molecular proportion in carbon tetrachloride, a mixture of two isomerical monobromo-derivatives is formed; one of these crystallises in minute, colourless, hexagonal pyramids, and decomposes at 150—160°; the other crystallises in monoclinic prisms, and decomposes at 145—146°; both have the composition $C_{15}H_{17}BrO_2$. When dihydroisosantinic acid is treated with bromine in the manner described, the product consists of silky, acicular crystals which have not yet been thoroughly examined. *Santinic* (dimethylnaphthylpropionic) acid, $C_{15}H_{16}O_2$, is prepared by boiling a glacial acetic acid solution of dihydrosantinic acid with a slight excess of iodine for about eight hours in a reflux apparatus. The product, after partial purification, is converted into the barium salt and decomposed with hydrochloric acid, when the pure acid is obtained. It crystallises from dilute alcohol in silky, lustrous needles, melts at 132—132·5°, dissolves readily in most organic solvents, but is insoluble in water. It is very soluble in alkalis and alkali carbonates, but is partially reprecipitated from its solutions by carbonic anhydride. On heating it above its melting point in an atmosphere of carbonic anhydride, it sublimes unaltered. The *silver* salt has the composition $C_{15}H_{15}AgO_2$; salts of the following metals —barium, calcium, strontium, magnesium, zinc, cadmium, lead, mercury, and manganese—can be obtained by precipitating their solutions with a solution of ammonium santinate. Hyposantonin or isohyposantonin may be substituted for dihydrosantinic acid in the preparation of santinic acid; when, however, isohyposantonin is used, the product is very impure. Santinic acid is dextrorotatory, $[\alpha]_D = +61{\cdot}88$ to $64{\cdot}37$. It probably has the constitution

$$\begin{array}{l} CH\cdot CMe{:}C\cdot CH{:}CH \\ \| \quad\quad | \quad\quad | \\ CH\cdot CMe{:}C\cdot CH{:}C\cdot CHMe\cdot COOH \end{array}.$$

Isosantinic acid, $C_{15}H_{16}O_2$, is obtained in a manner similar to santinic acid by the action of iodine on dihydroisosantinic acid. It melts at 132·5—133°. Its properties are the same as those of santinic acid, with the exception that it is inactive to light.

Dimethylethylnaphthalene, $C_{14}H_{16}$.—A mixture of this hydrocarbon with dimethylethyldihydronaphthalene, $C_{14}H_{18}$, is obtained on mixing dihydrosantinic or dihydroisosantinic acid (4 grams) with crystallised baryta (3 parts), drying, powdering, dehydrating at 250° in a vacuum, and distilling the residue at 260° in a vacuum. A small quantity of free hydrogen, equivalent to about one-third of the two hydrogen atoms attached to the naphthalene nucleus, passes over with the hydrocarbons. On treating the mixture with iodine, it is completely converted into dimethylethylnaphthalene, a clear, heavy, colourless, fluorescent oil which distils at 298—302°. On treating santinic and isosantinic acids in the manner described, the product consists entirely of dimethylethylnaphthalene, no hydrogen being evolved. No definite compounds could be obtained by the oxidation of either of the above hydrocarbons.

Paradimethylphthalic acid, $\begin{array}{l} CH{:}CMe\cdot C\cdot COOH \\ | \quad\quad\quad\quad \| \\ CH{:}CMe\cdot C\cdot COOH \end{array}$.—The anhydride of this acid is obtained by oxidising either of the dihydrosantinic or hyposantonic acids in alkaline solution with potassium permanganate, removing the excess of permanganate and the oxides of manganese, acidifying with sulphuric acid, and distilling. The anhydride is carried over by the steam, and a yellow, oily acid residue remains, from which a further quantity of the anhydride may be obtained by prolonged oxidation with nitric acid. It crystallises from ether in white, shining, rhombic plates, $a : b : c = 0{\cdot}425 : 1 : 0{\cdot}525$, melts at 143·5°, dissolves very sparingly in water, sparingly in absolute alcohol and ether, but very freely in light petroleum, benzene, or chloroform. In aqueous solutions, it is partly converted into the corresponding acid. It is readily soluble in hot alkaline hydrates and carbonates, and is not reprecipitated on acidification. On heating it above its melting point, it volatilises, forming a very light sublimate. On heating it with resorcinol and concentrated sulphuric acid, and making alkaline with soda or potash, a dichroic solution is obtained which is green by reflected, and brown or reddish-brown by transmitted, light. The acid is obtained by evaporating a solution of the anhydride in 90 per cent. alcohol in a vacuum in presence of paraffin. It crystallises from ether in monoclinic prisms, $a : b : c = 1{\cdot}312 : 1 : 0{\cdot}655$; $\beta = 87° 11' 46''$, melts at 96°, dissolves very freely in ether, alcohol, benzene, and chloroform, moderately in cold water, and very sparingly in light petroleum. On heating it above its melting point, it loses water and solidifies, the anhydride being formed. The *silver* salt, $C_{10}H_8Ag_2O_4$, forms shining crystals; the *ammonium* salt precipitates solutions of barium, magnesium, manganese, zinc, and lead.

On distilling a mixture of the anhydride with dry baryta, paradimethylbenzene passes over at about 400°.

The authors conclude by discussing the evidence for the constitutional formulæ given in the paper. S. B. A. A.

Constituents of Coto Bark. By G. Ciamician and P. Silber (*Ber.*, **25**, 1119—1138; compare Abstr., 1891, 578).—The formulæ previously suggested by the authors for hydrocotoïn and protocotoïn prove to be correct, as the trichlorinated derivative, $C_6Cl_3(OMe)_3$, on treatment with sodium in alcoholic solution, yields trimethoxybenzene [1 : 3 : 5]. The molecular weights of "dibenzoylhydrocoton" and "oxyleucotïn" are only half those indicated by the formulæ of Jobst and Hesse, since these compounds are identical with methylhydrocotoïn and methylprotocotoïn respectively. By the action of bromine in excess on methylhydrocotoïn, tribromotrimethoxybenzene [$(OMe)_3$ = 1 : 3 : 5] and benzoic acid are formed. Jobst and Hesse's "hydrocoton" prepared by the action of potash on "dibenzylhydrocoton" proves to be symmetrical trimethoxybenzene; the error in the vapour density determination is probably due to its being carried out at too low a temperature. Methylprotocotoïn, on treatment with bromine in excess, yields symmetrical tribromotrimethoxybenzene and piperonylic acid; the latter is converted quantitatively into 3 : 4-dihydroxybenzoic acid by fusion with potash.

The compound previously termed paracumarhydrin, obtained by the oxidation of protocotoïn, is acetopiperone, $C_6H_3Ac<^{O}_{O}>CH_2$ [O : O : Ac = 1 : 3 : 4], since, on oxidation with potassium permanganate in alkaline solution, it yields piperonylic acid and piperonylketonic acid.

On heating protocotoïn (5 grams) with potash (10 grams) and methyl alcohol (10 c.c.) in a sealed tube for 6—8 hours at 150°, a compound is obtained which crystallises from alcohol, melts at 154—154·5°, and has the formula $C_{13}H_7O_3(OMe)_3$; it is insoluble in water, dissolves in alkalis, and is reprecipitated by carbonic anhydride; a reddish-brown coloration is produced with ferric chloride, and a dark-green with nitric acid. By the action of acetic anhydride and anhydrous sodium acetate, the *diacetyl derivative*,

$$C_{13}H_5O(OMe)_3(OAc)_2,$$

is formed; it crystallises from alcohol in colourless needles, melting at 126—127°. The original compound, on treatment with methyl iodide and potash, yields a pentamethoxy-derivative,

$C_6H_2(OMe)_3{\cdot}CO{\cdot}C_6H_3(OMe)_2$ [$(OMe)_3$ = 1:3:5; CO = 1; $(OMe)_2$ = 3:4],

this compound crystallises from alcohol in small, colourless plates, melts at 157°, and is insoluble in alkalis. The *bromo-derivative*, $C_{13}H_4BrO(OMe)_5$, is deposited from alcohol in prisms melting at 144°; by the action of bromine in excess symmetrical tribromotrimethoxybenzene and bromoveratric acid are formed, thus proving its composition.

Two compounds are obtained by the action of potash (20 grams) and methyl alcohol (20 c.c.) on methylprotocotoïn (10 grams) for six hours at 130—140°; the one is identical with the compound described above (m. p. 154·5°); the second, which is separated by

fractional crystallisation from alcohol, melts at 180°, is soluble in alkalis with a yellow colour, and gives a greenish-yellow coloration with nitric acid; its formula is $C_{13}H_6O_2(OMe)_4$; on treatment with methyl iodide and potash, the pentamethoxy-compound (m. p. 157°); see above) is formed; the acetyl derivative crystallises from alcohol and melts at 170°.

On treating protocotoïn with potash and ethyl alcohol under pressure at 155°, an *ethoxy-derivative*,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot C_6H_3(OEt)\cdot OH,$$

is formed, and crystallises from alcohol in yellow prisms, melting at 150—151°; it resembles the trimethoxy-compound in general properties. The *diacetyl derivative*, $C_{13}H_5O(OMe)_2(OAc)_2\cdot OEt$, crystallises in hexagonal plates which melt at 118°. On treatment with methyl iodide and potash, a tetramethoxyethoxy-compound,

$$C_6H_2(OMe)_3\cdot CO\cdot C_6H_3(OMe)\cdot OEt,$$

is formed, melting at 162°. J. B. T.

Aristolochin. By J. Pohl (*Chem. Centr.*, 1892, i, 42—43; from *Arch. expt. Path. Pharm.*, **29**, 282—301).—*Aristolochin*, $C_{32}H_{22}N_2O_{13}$, a poisonous constituent of the seeds and roots of the Aristolochiaceæ, has been separated and examined by the author. The ground-up seeds and roots were first extracted with light petroleum, which separates an oil and a physiologically inactive substance. The residue was then exhausted with alcohol (96 per cent.), the alcohol distilled off, and the residue dissolved in water. Sulphuric acid precipitated a yellow substance, which was dried, and exhausted first with light petroleum, and then with ether or alcohol. The latter separates the aristolochin, which crystallises as the solvent evaporates. With concentrated sulphuric acid, it gives a dark-green coloration; fused with potash, the coloration is purple-red; it is precipitated by the alkalis and lead acetate; it does not reduce cupric oxide. Treated with glacial acetic acid and zinc-dust, a product is obtained which is not bitter, and the alcoholic solution of which has a green fluorescence. Aristolochin forms a crystalline salt with barium.

Physiologically it acts similarly to aloïn, but much more energetically. J. W. L.

The Chlorophyllic Substances of the Pericarp of the Grape. By A. Étard (*Compt. rend.*, **114**, 231—233).—The dry material obtained by the desiccation of 100 kilos. of grape skins is treated with carbon bisulphide. From 0·3 to 1 kilo. of extract is obtained; it consists essentially of chlorophyll and some of its accompanying substances, and is free from sugars, gums, and salts. The mass is green, and has the consistency of tallow. By distillation in a vacuum it yields 85 per cent. of acids, consisting of palmitic acid and a small proportion of unsaturated liquid acids. By hydrolysis with alcoholic potash, free from soda, dilution with water, and filtration, a white substance soluble in ether is obtained. The name *œnocarpol* is proposed for this compound. It forms long needles melting at 304°;

its solution in ether has a rotation $\alpha = +60{\cdot}8°$. By heating with acetic anhydride in sealed tubes at 130°, the acetyl derivative melting at 215° is obtained. The formula of œnocarpol is $C_{26}H_{39}(OH)_3,H_2O$. On heating, water is first lost, then, at 405° (Baudin's thermometer) a hydrocarbon $C_{26}H_{36}$ distils over. This substance has a tenacious odour, and appears, like the polyterpenes, to be balsamic in character. It slowly combines with water to give fine crystals, fusing at 175°, of the composition $(C_{26}H_{36})_2,H_2O$. With potash, œnocarpol gives brilliant, infusible, slightly soluble needles, of a compound having the composition $C_{26}H_{39}(OH)_3,KOH,H_2O$, a formula which may be written $C_{26}H_{41}(OH)_4{\cdot}OK$. From the potassium salt, metallic derivatives have been obtained, having the formulæ $2(C_{26}H_{42}O_3,H_2O),3AgOH$ and $2(C_{26}H_{42}O_3,PbO),Pb(OH)_2$, which again yield œnocarpol hydrate on treatment with hydrogen sulphide. By oxidation with chromic acid, œnocarpol yields an amorphous acid, $C_{26}H_{42}O_5$, which saturates alkaline carbonates, and yields a balsam on distillation.

On treating the carbon bisulphide extract with lead acetate and passing a current of hydrogen sulphide, œnocarpyl palmitate may be extracted by means of neutral solvents; it fuses at 272°, and is saponifiable. W. T.

Organic Phosphorus Compounds. By P. Heermann (*J.pr. Chem.* [2], **45**, 296—300).—The author records the failure of his attempts to produce compounds of the type of pyrroline in which phosphorus shall take the place of nitrogen. The action of hydrogen phosphide on mucic acid and of the same gas, or of phosphonium iodide, on acetonylacetone and on dixylylethylene diketone were tried, but with negative results. Messinger and Engels have studied the action of hydrogen phosphide on aldehydes (Abstr., 1888, 441; 1889, 35).

A. G. B.

Nomenclature of Compounds containing Nitrogenous Nuclei. By O. Widman (*J. pr. Chem.* [2], **45**, 200—212).—The author criticises Hantzsch's system of nomenclature (this vol., p. 312), and points out its weaknesses as compared with his own system. He also replies to some criticisms of Knorr (Abstr., 1889, 1218). A. G. B.

γ-Bromoquinoline. By A. Claus (*J. pr. Chem.* [2], **45**, 222—236).—Claus maintains that Decker's case for the 3′-position of the bromine in this bromoquinoline (this vol., p. 630) is not made out. He is not satisfied that Baeyer and Bloem's carbostyril (m. p. 266°, Abstr., 1883, 196) is 4′-bromocarbostyril, and is of opinion that the evidence which he quotes is rather in favour of its being 3′-bromocarbostyril, in which case Decker's compound (m. p. 253°, *loc. cit.*) would be 4′-bromocarbostyril. Analogy between the reactions of the substitution derivatives of pyridine and those of quinoline must not be pressed as an argument in favour of the orientation of the latter being in the pyridine ring, because the influence exerted on such reactions by the existence of the benzene ring in quinoline is known to be considerable.

The oxidation of the bromoquinoline in question yields a bromopyridinedicarboxylic acid, which readily loses carbonic anhydride when heated, forming a bromopyridinecarboxylic acid (Abstr., 1887, 159), which is shown to be a bromonicotinic acid, inasmuch as it yields nicotinic acid (m. p. 228°) by treatment with sodium amalgam; there is thus little doubt that the dicarboxylic acid is a quinolinic acid derivative, and that the bromine is in the 4′-position in both acids. The question has been even more definitely settled by the direct bromination of nicotinic acid in a chloroform solution; such a reaction would be expected by *a priori* reasoning to yield 3′-*bromonicotinic acid*. The acid, thus prepared, crystallises in prisms, melts at 275°, and is fairly soluble in cold water, whilst the acid prepared from the bromoquinoline, as referred to above, crystallises in laminæ, melts at 183°, and is very sparingly soluble in cold water (Abstr., 1887, 159). The difference between these two acids is sufficiently marked to enable us to definitely ascribe the constitution 3′-bromo- and 4′-bromo-nicotinic acid respectively to them (this vol., p. 630).

The "so-called γ-bromoquinoline and its derivatives" thus regain the position from which it was attempted to thrust them.

3′ : 4′-Dibromonicotinic acid crystallises in colourless prisms, melts at 243°, and is sparingly soluble in cold water. A. G. B.

Halogen Alkyl Compounds of Hydroxyquinolines and their Decomposition by Alkalis and by Silver Oxide. By A. Claus, H. Howitz, C. Massan, and G. Raps (*J. pr. Chem.* [2], **45**, 237—260; compare Abstr., 1891, 1252).—2-*Hydroxyquinoline methiodide*, $C_9NH_6{\cdot}OH,MeI$, is obtained by heating a mixture of 2-hydroxyquinoline and methyl iodide for several hours in a sealed tube at 130°; after treatment with animal charcoal, the product crystallises from aqueous alcohol in aggregates of lustrous needles and prisms; it melts at 251°. The *methochloride* can be prepared by decomposing the methiodide in aqueous solution by silver chloride; it crystallises in flat, yellow needles, and melts at 238°. The *methohydroxide*, $C_9NH_6{\cdot}OH,MeOH$, is obtained by treating either of these methohalides with silver oxide or potassium hydroxide; it crystallises in very hygroscopic needles, and dissolves very easily in water and alcohol, but not in ether and allied solvents; the aqueous solution is yellowish-red by transmitted light, and shows a green fluorescence by reflected light; it is strongly alkaline. It is to be noted that there is no difference between the action of silver oxide and that of potassium hydroxide on these 2-hydroxyquinoline derivatives (compare Abstr., 1891, 1252).

Two sulphonic acids are obtained when isoquinoline is sulphonated (compare Hoogewerf and Van Dorp, Abstr., 1887, 505); they are temporarily distinguished as I and II. When the sulphonation is effected with 40 per cent. anhydrosulphuric acid at 180—200°, the acid I is the chief product; at 300°, however, the acid II is almost exclusively produced. With 60 per cent. anhydrosulphuric acid at 110—112°, the acid I is again the larger product. The acids are separated by the fractional crystallisation of their barium salts, of which the salt I is the less soluble, and crystallises first in long,

lustrous, colourless needles. The salt II forms aggregates of small needles. Both salts contain water of crystallisation, which is not completely expelled below 200°. The corresponding hydroxyisoquinolines are obtained by fusing these salts with sodium or potassium carbonate, dissolving the melt in water, and acidifying with acetic acid; the hydroxyisoquinoline separates as a grey or brown powder, and is purified by boiling its alcoholic solution with animal charcoal.

Hydroxyisoquinoline I is a nearly colourless powder which dissolves easily in alcohol, sparingly in water and ether, and not at all in light petroleum and benzene; it sublimes in the form of colourless needles, and melts with decomposition at 230°; it does not volatilise with steam. The *hydrochloride* and *sulphate* form sulphur-yellow needles; the *platinochloride* crystallises, with 7 mols. H_2O, in long, brilliant, orange-red needles and prisms; the *methiodide* forms long, straw-yellow, anhydrous needles, and melts at 239° with decomposition; the *methochloride*, prepared from the methiodide by the action of silver chloride, forms yellow crystals, blackens at 220°, melts at 256—258°, and dissolves in water; the *methosulphate*, from the methiodide and silver sulphate, crystallises in greenish-yellow, flat needles and laminæ, which melt in their water of crystallisation at 100°, and decompose at 270—275°. By treatment with silver oxide, potassium hydroxide, or barium hydroxide, any of the above metho-derivatives yields the *methohydroxide;* this crystallises from water in long, reddish-yellow plates, and from alcohol in flat prisms; it melts with decomposition, and dissolves easily in water and alcohol, but not in ether; its solutions are strongly alkaline, and absorb carbonic anhydride, but no carbonate could be isolated.

Hydroxyisoquinoline II is similarly isolated. From alcohol it separates as a white, crystalline powder, and it is obtained in the same form by sublimation; it melts at 184°, and is not volatile with steam. In its other properties, it resembles the base I. The *hydrochloride*, *sulphate*, and *platinochloride* were prepared. The *methiodide* crystallises in long, brilliant, yellow needles (with 1 mol. H_2O), and melts in its water of crystallisation at about 100°, subsequently solidifying and melting finally with decomposition at 224°. The *methochloride* forms sulphur-yellow crystals, melts at 216—218°, and is freely soluble in water. The *methosulphate* melts first in its water of crystallisation at 100°, and finally with decomposition at 230°. The *methohydroxide* crystallises with water in which the crystals melt at 85—90°; when dry, it softens at 130°, but does not melt until about 180°, when it forms a thick, black liquid. There is thus no difference between the action of potassium hydroxide and that of silver oxide on these hydroxyisoquinoline derivatives, quaternary ammonium bases being produced in each case.

4-Hydroxy-3-chloroquinoline is obtained from the corresponding amidochloroquinoline by diazotising and treating the diazo-derivative with dilute cuprous chloride solution. It crystallises in pale-yellow needles, melts at 183—184°, sublimes, and is freely soluble in water, alcohol, ether, and chloroform. The *methiodide* crystallises in short, yellow needles, and melts with decomposition at 199—201°. The

methochloride crystallises in very soluble, yellow needles, which melt in their water of crystallisation at 100—110°, and when anhydrous at 235—240°.

The action of potassium hydroxide and of silver oxide on 4-hydroxy-3-chloroquinoline methiodide differ. When a strong solution of the methiodide is shaken with ether and a dilute solution of potassium hydroxide, the ether dissolves the liberated base and leaves it, on evaporation, as a thick, yellow oil, which rapidly oxidises in the air after the fashion characteristic of the alkylenequinolinium bases (compare Abstr., 1891, 1252; and 1890, 1323). When a strong solution of potassium hydroxide is used, the potassium compound of the base crystallises from the liquid, and is not dissolved by the ether, but the addition of water dissociates it, and the ether dissolves the base. When the ethereal solution is shaken with dilute hydrochloric acid, it is decolorised, and crystals of the methochloride described above are obtained from the hydrochloric acid solution. The authors regard this base as a *methylenehydroxyquinolinium* [CH_2 : Cl : OH = 1′ : 3 : 4], and point out that the presence of a hydroxyl group in the 4-position does not influence the behaviour of the quinoline alkyl derivatives with potassium hydroxide, as do hydroxyl groups in 3- and 2-positions (compare Abstr., 1891, 1252, and above). They regard this fact as being especially important with respect to the 2-position, for considering quinoline a derivative of a benzene ring, the 4- and 2-positions are both meta-positions with respect to the nitrogen, and might be expected to have equal values. Some remarks as to the alkyl derivatives of some cinchona alkaloïds being of the nature of quinolinium bases are here made, but will be given more fully in a paper which will shortly appear in the *Annalen*.

The action of silver oxide on 4-hydroxy-3-chloroquinoline methiodide produces the quaternary ammonium base, the corresponding *methohydroxide;* this crystallises in large, brilliant, red, transparent prisms (with H_2O), blackens at 170°, and melts with decomposition at 240°; it is insoluble in ether, and is converted into the methochloride described above when treated with hydrochloric acid.

A recantation here follows: 1-hydroxyquinoline methiodide yields the same quaternary ammonium base whether acted on by excess of alkali or by silver oxide, the contrary statement made in *J. pr. Chem.* [2], **43**, 510 (Abstr., 1891, 1252) being an error. The "intermediate iodide" of Lippmann and Fleissner, obtained by treating 1-hydroxyquinoline methiodide (2 mols.) with potassium hydroxide (1 mol.) (Abstr., 1890, 1323), crystallises in brilliant, thin, orange-yellow needles, and not in red crystals as heretofore stated. When silver oxide is used, no "intermediate iodide" can be obtained.

1-*Hydroxyquinoline methohydroxide* forms red, prismatic crystals (with 1 mol. H_2O); it softens at 110°, melts at 115°, and dissolves in water, alcohol, and chloroform; in its other properties, it resembles the methohydroxides described above.

No "intermediate product" is obtained when 1-hydroxyquinoline methosulphate is treated with barium hydroxide or potassium hydroxide; but barium hydroxide yields the "intermediate iodide" when it acts on the methiodide. A. G. B.

Action of Alkalis on Alkyl Iodides of the Quinoline and Acridine Series. By H. Decker (*J. pr. Chem.* [2], **45**, 161—200). —With regard to the nomenclature used in this paper, it should be noted that Claus (this vol., p. 875) does not admit the orientation 3′-bromoquinoline ascribed by Decker (this vol., p. 630) to his 4′-bromoquinoline. "α-Quinolones" (2′-quinolones) is the name given by the author to derivatives of the lactam formula for carbostyril.

The work described below shows that La Coste's formula, $(C_9H_6BrNMe)_2O$ (Abstr., 1882, 980), for the compound obtained by the action of silver oxide on 3′-bromoquinoline is not even empirically correct, so that his view as to its constitution being that of an ammonium oxide is also invalid.

Bromomethylquinolone, $C_6H_4<\begin{matrix}N—CO\\ CH:CBr\end{matrix}$ [Br : Me : O = 3′ : 1′ : 2′], is prepared by adding an alkali to a saturated solution of 3′-bromoquinoline methiodide in water; a precipitate is formed which rapidly absorbs oxygen from the air and is converted into the new compound, of which La Coste's "ammonium oxide" (*loc. cit.*) was an impure specimen; by adding potassium ferricyanide to the alkali and gradually pouring in the solution of 3′-bromoquinoline methiodide, the compound may be obtained directly. It melts at 149° (not 147°). It is a very feeble base, forming unstable, crystalline salts; no platinochloride could be obtained. Its constitution is settled by the fact that it can be easily obtained by heating dry sodium 3′-bromocarbostyril (this vol., p. 630) with the calculated quantity of methyl iodide in benzene for three hours at 140°.

Bromethylquinolone [Br : Et : O = 3′ : 1′ : 2′] is similarly obtained; it crystallises in large, well-formed tables, melts at 116°, and is more soluble in alcohol and benzene than the methyl derivative.

The author considers that the mechanism of the change involved in the reaction between 3′-bromoquinoline methiodide, alkalis, and oxygen consists in (1) the formation of a phenol containing the group $N<\begin{matrix}Me\\ OH\end{matrix}$, (2) the oxidation of this group to $N\leqslant\begin{matrix}Me\\ O\end{matrix}$ simultaneously with the oxidation of the 2′-hydrogen atom, and (3) the immediate elimination of the oxygen from the group $N\leqslant\begin{matrix}Me\\ O\end{matrix}$, with the production of the quinolone. In support of (3) he quotes the instability of compounds containing the group $R_3{:}N{:}$, such as the tertiary amine dibromides, $R_3{:}N{:}Br_2$, which readily yield tertiary amines, $R_3{:}N$, when treated with alkalis. He further compares the reaction with the formation of pseudochlorocarbostyril from quinoline and hypochlorous acid (Abstr., 1886, 370), in which he considers the group $N<\begin{matrix}Cl\\ OH\end{matrix}$ to be first formed and subsequently oxidised, together with the 2′-hydrogen atom, by more hypochlorous acid. As further support, he points out that 1-substituted quinolines yield no carbostyril with hypochlorous acid (Abstr., 1888, 502; 1891, 1249). The action of methyl iodide on sodium 3′-bromocarbostyril consists in the formation of the methiodide containing the group $N<\begin{matrix}Me\\ I\end{matrix}$, and

the subsequent combination of the iodine atom of this group with the sodium atom in the 2′-sodoxyl group, resulting in the elimination of sodium iodide.

2-*Bromomethylquinolone*, obtained by treating 2-bromoquinoline methiodide (Abstr., 1889, 280) with an alkali and potassium ferricyanide, crystallises from alcohol in lustrous needles, and melts at 173°; the *platinochloride* was prepared.

3-*Bromomethylquinolone* melts at 145°, and 4-*bromo*-1′-*methyl*-2′-*quinolone* at 146—147°; they resemble the other isomerides in properties.

4-*Nitromethylquinolone* is obtained by the action of alkaline potassium ferricyanide on 4-nitroquinoline methiodide; it crystallises from alcohol in lustrous, yellow needles, melts at 167°, sublimes unchanged, dissolves in benzene and ether, and yields a *platinochloride*. As it is not identical with the nitromethylcarbostyril (m. p. 181°; Abstr., 1885, 1235) prepared from the so-called γ-nitrocarbostyril (Abstr., 1885, 1139), the orientation of the nitro-group in the latter must be either 2- or 3-.

4-*Nitroethylquinolone* forms yellow aggregates of crystals, melts at 135°, and is more soluble in alcohol, benzene, and water than the methyl derivative.

4-*Nitrodimethylquinolone* [$NO_2 : Me_2 : O = 4 : 3 : 1' : 2'$], prepared by the action of alkaline potassium ferricyanide on 3 : 4-methylnitroquinoline (nitroparatoluquinoline; Abstr., 1891, 325, crystallises from alcohol and melts at 192°; it dissolves in hydrochloric acid and gives a *platinochloride*.

Nitrobromoquinolinemethylium hydroxide [$NO_2 : Br : MeOH = 4 : 3' : 1'$] has been already obtained in an impure condition, and described as ananitro-γ-bromomethylquinoline (Abstr., 1889, 728); it crystallises from ether at −20° in long, yellow needles; it is permanent in the dark, but rapidly decomposed in light; it dissolves in excess of alkali with a red colour and apparently without decomposition, for ether or benzene decolorises the solution by extracting the base. By oxidation, it yields 4-*nitro*-3′-*bromomethylquinolone*; this crystallises in yellow, flat needles, sublimes unchanged, and melts at 232°. Reference has been already made (Abstr., 1889, 728) to the crystalline compounds which 4-nitro-3′-bromoquinolinemethylium hydroxide makes with the alcohols when crystallised from them. These compounds do not contain the alcohol as "alcohol of crystallisation," but are definite "alcoholates," containing an alkyl or other alcohol radicle in the place of the hydroxyl hydrogen, their formation being accompanied by elimination of water; they can be recrystallised from ether, benzene, chloroform, and the corresponding alcohol unchanged. They are insoluble in water, but are gradually converted by it into the hydroxide and corresponding alcohol; in some cases, another alcohol will perform the same function as water and cause the replacement of the existing radicle by the new alcohol radicle. The 4-nitro-3′-bromoquinolinemethylium ethoxide has been already described (*loc. cit.*); its crystallography is here detailed. The *methoxide* forms brown crystals, blackens gradually in light, melts at 81° to a thick, yellow oil which gradually solidifies again, and decomposes with

blackening at 120°; the *normal propoxide*, the *isopropoxide*, the *allyloxide* (m. p. 85°), the *isobutoxide* (m. p. 70°), the *normal butoxide* (m. p. 55°), the *trimethylcarbinyloxide* (m. p. 127° with decomposition), the *amyloxide* (m. p. 65°), and the *benzyloxide* (m. p. 120°) were obtained; the crystallographic measurements of most of them are given.

4-*Nitro*-3-*bromoquinolinemethylium hydroxide*, obtained by precipitating a saturated solution of 4-nitro-3-bromoquinoline methiodide with ammonia, did not crystallise, nor could its ethoxide be obtained otherwise than as a thick, yellow oil. It is easily oxidised to 4-*nitro*-3-*bromomethylquinolone*, which crystallises in needles, melts at 203°, and dissolves in most solvents.

Nitro-4-*bromomethylquinolone*, obtained from nitro-4-bromoquinoline, crystallises in needles, and melts at 220°.

Acridinemethylium hydroxide, $C_{10}H_9NMeOH$, is a white precipitate, produced by adding sodium hydroxide to a solution of acridine methiodide; it is exceedingly unstable, immediately oxidising to *methylacridone*, $C_6H_4<^{CO-}_{NMe}>C_6H_4$. This compound crystallises from alcohol in large, yellow needles, and melts at 190°; it dissolves in alcohol with a blue fluorescence, and in acids, from which it is precipitated unchanged by water; it is sparingly soluble in hot water and sublimes unchanged; a *platinochloride* was isolated.

Bernthsen (Abstr., 1883, 1133) described the compound obtained by crystallising from alcohol the product of the reaction between phenylacridine methiodide and sodium hydroxide, and named it phenylacridinemethylium hydroxide; this substance is really *phenylacridinemethylium ethoxide* (m. p. 108°), $C_6H_4<^{-CPh--}_{NMe(OEt)}>C_6H_4$. The *hydroxide* is obtained by crystallising the above-mentioned product from hot benzene; it forms large, brilliant tables which melt at 140°, dissolves in most solvents except water, and yields an unstable *carbonate;* attempts to obtain an oxidation product analogous to the 2′-quinolones were ineffectual. The *benzyloxide* melts at 133°.

A. G. B.

Oxidation of Benzoyltetrahydroquinaldine, and Nitro-derivatives of the same. By G. Walter (*Ber.*, 25, 1261—1270). —Benzoyltetrahydroquinaldine is prepared by hydrogenising quinaldine with tin and hydrochloric acid, and treating the resulting tetrahydro-derivative by the Baumann-Schotten method; it crystallises in large, four-sided prisms or delicate needles, melts at 118°, is soluble in most organic solvents, and is hydrolysed by protracted boiling with hydrochloric acid. When it is boiled with alkaline potassium permanganate solution, and the filtrate evaporated and acidified with hydrochloric acid, carbonic anhydride is evolved and a gelatinous mass separates, from which boiling water extracts benzoic acid, whilst oxalic acid is present in the supernatant liquid. The above-mentioned mass is boiled with water and magnesia, filtered while hot, and the filtrate acidified, when *benzoylorthamidophenylacrylic acid*,

$$COOH{\cdot}C_2H_2{\cdot}C_6H_4{\cdot}NHBz,$$

separates, and is crystallised from alcohol; it forms thick needles,

melts at 191—193°, is sparingly soluble in hot water, and slowly reduces Fehling's solution in the cold. When the acid is heated with concentrated hydrochloric acid at 160—180°, or carefully fused with potash, indole and benzoic acid are produced. When administered to a dog, no increase of indoxyl was recognised in the urine, but the animal was lamed in the hinder extremities.

The excess of magnesia from which magnesium benzoylorthamidophenylacrylate is filtered contains the salt of benzoylanthranilic acid; the free acid remains when the mixture is treated with hydrochloric acid, and melts at 177°, as stated by Doebner and v. Miller (*Ber.*, **19**, 1196).

When benzoyltetrahydroquinaldine is allowed to remain in contact with fuming nitric acid for several days, a *mononitro*-derivative, which crystallises from alcohol in yellow needles and melts at 149°, is obtained; whilst, if heated at 50—60° with fuming nitric acid, a *dinitro*-derivative, which crystallises from alcohol in small, yellow needles and melts at 169—170°, is produced.

Metanitrobenzoyltetrahydroquinaldine, $C_{10}NH_{12}\cdot CO\cdot C_6H_4\cdot NO_2$, is prepared by shaking tetrahydroquinaldine with metanitrobenzoic chloride and aqueous sodium hydroxide; it crystallises in pale-yellow leaflets, and melts at 114°. When treated with concentrated nitric acid at 20—50°, a dinitro-derivative melting at 163—164° is obtained, whilst heating it at 90—100° with concentrated nitric acid yields a trinitro-derivative, which crystallises in long, delicate, sulphur-yellow needles, and melts at 184—185°. A. R. L.

Preparation of Isoquinoline from Naphthalene. By E. Bamberger and M. Kitschelt (*Ber.*, **25**, 1138—1147; compare this vol., p. 857).—*Lead isocumarocarboxylate*, $CH\ll^{C_6H_4-COO}_{C(OH)\cdot COO}>Pb$, is insoluble and amorphous.

Isocarbostyrilcarboxylic acid, $C_6H_4<^{CO\cdot NH}_{CH:C\cdot COOH}$, is prepared by dissolving isocumarinecarboxylic acid in ammonia and acidifying the solution; it crystallises in slender, colourless, silky, lustrous needles which melt at 320° with previous decomposition; the acid is soluble in alcohol, acetone, and concentrated mineral acids, and is reprecipitated on the addition of water; with ferric chloride, an intense yellowish-red coloration is produced. The *silver* and *mercuric* salts are gelatinous; the *lead*, *copper*, *barium*, *zinc*, *cadmium*, *calcium*, and *ammonium salts* are crystalline; the acid is not acted on when heated with alkalis or acetic chloride, but is deposited from the latter in small, pale yellow needles, quite different in appearance from the ordinary crystals, and these are unaffected by repeated crystallisation from alcohol. On heating the acid below its melting point, or by heating the silver salt at 150—160°, *isocarbostyril*, $C_6H_4<^{CO\cdot NH}_{CH:CH}$, is formed, and may be purified by washing with dilute soda; it crystallises from benzene and readily sublimes, forming lustrous needles which melt at 208—209°; the compound is soluble in concentrated

mineral acids, and the solutions do not fluoresce ; it gives precipitates with solutions of phosphotungstic acid, phosphomolybdic acid, potassium bismuthiodide, and mercuric nitrate. Isoquinoline is obtained by heating isocarbostyril with zinc dust in excess.

The authors point out that β-naphthol yields 75 per cent. of β-naphthaquinone, and that the latter gives, according to Zincke's method, 70—75 per cent. of dihydrohydroxyisocumarinecarboxylic acid, whilst the preparation of isocumarinecarboxylic acid, isocarbostyrilcarboxylic acid, isocarbostyril, and isoquinoline proceed almost quantitatively. J. B. T.

Julole. By W. Kaiser and A. Reissert (*Ber.*, **25**, 1190—1192, and 1193—1201).—To determine if the reaction which takes place between ethyl acetoacetate and tetrahydroquinoline (Abstr., 1891, 736) is a general one, the authors have examined the behaviour of tetrahydroquinoline and tetrahydroquinaldine towards ethyl ethylacetoacetate and ethyl benzoylacetate, and find that only in the case of tetrahydroquinoline and ethyl ethylacetoacetate is the condensation product formed in sufficient quantity to be isolated.

α₁-Keto-β₁-ethyl-γ₁-methyljuloline is obtained by gently boiling a mixture of molecular proportions of ethyl ethylacetoacetate and tetrahydroquinoline for one hour in a reflux apparatus. The cold product is poured into twice the volume of ice-cold concentrated sulphuric acid, then poured into water and excess of alkali added ; the unaltered hydroquinoline is separated by steam distillation. The compound is obtained as a finely-divided, yellowish-brown precipitate. It crystallises from petroleum in beautiful, white needles, melts at 80°, and is easily soluble in alcohol, ether, acetic acid, chloroform, benzene, and mineral acids. It is also soluble in hot water, but does not crystallise from this solvent. When treated with phosphorus pentachloride, it yields an indigo-blue dye containing chlorine ; this easily decomposes with evolution of hydrogen chloride and forms a dye insoluble in water (this vol., p. 498). The *picrate* crystallises in yellow needles and melts at 89°.

Bromo-α₁-keto-β₁-ethyl-γ₁-methyljuloline, $C_{15}H_{16}NO{\cdot}Br$, is obtained by adding an aqueous solution of bromine (1 mol.) to the preceding compound dissolved in hydrochloric acid, and heating until the colour of the bromine has disappeared. It crystallises from dilute alcohol in needles, melts at 140°, is easily soluble in alcohol, ether, benzene, chloroform, and acetic acid, but is insoluble in petroleum and water.

Nitroketoethylmethyljuloline, $C_{15}H_{16}NO{\cdot}NO_2$, is obtained by warming ketoethylmethyljuloline with concentrated nitric acid until a tarry precipitate begins to form, and then pouring into water. It crystallises from dilute alcohol in yellow leaflets, melts at 168°, and is easily soluble in hot alcohol and acetic acid, sparingly so in ether benzene, and chloroform, and insoluble in petroleum and water.

Whilst only about 12 per cent. of the theoretical yield of ketomethyljuloline is obtained by the condensation of ethyl acetoacetate and tetrahydroquinoline, the condensation of ethyl malonate and tetrahydroquinoline takes place much more readily, and a 50 per cent. yield is obtained.

α_1-*Keto*-γ_1-*hydroxyjuloline* is obtained by gently boiling molecular proportions of tetrahydroquinoline and ethyl malonate for about 7 hours in a reflux apparatus. The alcohol which is formed is then distilled off together with the unaltered malonate; in about half an hour, a second reaction sets in and alcohol again comes over. On cooling, a yellow, crystalline mass is obtained, which is washed with ether and alcohol. After boiling with animal charcoal, it crystallises from acetic acid in lustrous, white needles, melts about 300° with decomposition, and is soluble in hot acetic acid and concentrated mineral acids, sparingly so in hot alcohol, almost insoluble in ether and benzene, and insoluble in water, chloroform, petroleum, and dilute acids. The *hydrochloride* crystallises in long, white needles. The *barium* salt, $(C_{12}H_{10}NO_2)_2Ba$, is obtained as a finely-divided precipitate by adding barium chloride to a solution of the sodium salt, and, like the other salts of this compound, cannot be crystallised from water. Ketohydroxyjuloline, when heated with phenylhydrazine (1 mol.) in 50 per cent. acetic acid for 3—4 hours, yields a compound of the formula $C_{12}H_{11}NO_3$, which melts at 260°, does not reduce Fehling's solution, and is easily soluble in alcohol and hot acetic acid. When treated with 2 mols. of phenylhydrazine, it remains unchanged. The mother liquors of the compound melting at 260° were extracted with ether, and yielded a substance which crystallises in lustrous needles, melts at 125°, reduces Fehling's solution, and evolves phenylhydrazine when boiled with sodium hydroxide.

α_1-*Keto*-γ_1-*chlorojuloline*, $C_{12}H_{10}NOCl$, is obtained by heating ketohydroxyjuloline with phosphorus pentachloride and phosphorus oxychloride for half an hour at 120°. It crystallises in reddish needles, melts at 135°, is easily soluble in alcohol, ether, acetone, acetic acid, benzene, and concentrated acids, and insoluble in petroleum and alkalis.

α_1-*Keto*-γ_1-*benzoxyjuloline*, $C_{19}H_{15}NO_3$, is obtained by shaking the sodium salt of ketohydroxyjuloline with benzoic chloride, treating the mixture with alkali, and crystallising the insoluble portion from acetic acid. It crystallises in long, white needles, melts at 151°, and is insoluble in hot alcohol, acetone, acetic acid, and benzene, sparingly so in ether and petroleum, and insoluble in water, alkalis, and dilute acids.

α_1-*Keto*-β_1-*nitroso*-γ_1-*hydroxyjuloline* is obtained by adding the calculated quantity of potassium nitrite to a solution of the ketone in acetic acid; on diluting with water, about two-thirds of the ketone is precipitated unaltered; on adding alkali to the filtrate, a beautiful, green precipitate is obtained, which is soluble in dilute acids. If the filtrate be acidified and extracted with ether, the nitroso-compound is obtained. It crystallises in red needles, melts at 158° with decomposition, is soluble in hot water, alcohol, ether, benzene, and dilute acids, and yields a green solution with alkali hydroxides and carbonates. E. C. R.

Formation of Pyrazole Derivatives from the Dichlorhydrins and Tribromhydrin. By U. Alvisi (*Gazzetta*, 22, i, 158—168).—A solution of phenylhydrazine (12·5 grams) and β-dichlorhydrin (5 grams) in benzene (20 grams), when boiled for 12 hours, deposits a

mixture (1·3 grams) of ammonium chloride and phenylhydrazine hydrochloride. This deposit is filtered off, and the solvent evaporated; on heating the residue at 137—140°, ammonia and water vapour are evolved, leaving a resinous mass which is extracted with ether. The residue consists of ammonium chloride, and the hydrochloride of a base which has not yet been studied. The ethereal solution is shaken with dilute hydrochloric acid, which extracts aniline, and the ether distilled off. The residue, on distillation, is found to be 1-phenylpyrazole.

When a benzene (20 grams) solution of α-dichlorhydrin (12 grams) and phenylhydrazine (30·5 grams) is boiled for 12 hours in a reflux apparatus, much ammonia is given off, and 1-phenylpyrazole is formed.

Similarly, on heating tribromhydrin (28 grams) and phenylhydrazine (42 grams), dissolved in benzene (25 grams), reaction readily occurs, and 1-phenylpyrazole is obtained. W. J. P.

New Series of Platinum Compounds derived from the Pyrazoles. By L. Balbiano (*Real. Accad. Linc.*, **7**, ii, 26—34).—The author has previously shown (Abstr., 1890, 1009) that pyrazole platinochloride loses its water of crystallisation at 100°, and on further heating at 200—210°, 4 mols. HCl are eliminated, and a substance of the composition $(C_3N_2H_3)_2PtCl_2$ is obtained. Analogous compounds prepared from substituted pyrazoles are now described.

On heating 1-phenylpyrazole platinochloride, it first loses its water of crystallisation, and then at 150—160° hydrogen chloride is evolved, leaving a substance of the composition $(C_3H_2N_2Ph)_2PtCl_2$. It is a light-yellow powder, sparingly soluble in boiling alcohol and water, insoluble in cold water and acids. It is not altered by heating in a closed tube with fuming hydrochloric acid at 100° for 3—4 hours.

1-Orthotolylpyrazole platinochloride, when heated at 160—170°, yields a compound of the composition $(C_3H_2N_2{\cdot}C_7H_7)_2PtCl_2$. It is a pale-yellow powder insoluble in water, sparingly soluble in boiling alcohol. It is purified by precipitating its boiling alcoholic solution with water. An isomeride of this substance having similar properties is obtained by heating 1-paratolylpyrazole platinochloride at 180°.

1 : 4 : 5-*Phenylmethylethylpyrazole platinochloride*,

$$(C_3HMeEtN_2Ph)_2,H_2PtCl_6 + 2H_2O,$$

is prepared by dissolving the pyrazole obtained from propionylpropaldehyde in hydrochloric acid, and treating with a concentrated acid solution of platinic chloride. It crystallises in beautiful, yellowish-red laminæ, and on heating at 160° yields a substance of the composition $(C_3MeEtN_2Ph)_2PtCl_2$, as a pale-yellow powder, insoluble in water and almost so in alcohol.

1 : 3 : 5-Phenyldimethylpyrazole platinochloride has been described by Knorr as crystallising with 4 mols. H_2O, the last of which it loses at 130—140°. The author finds that it contains only 2 mols. H_2O, which are eliminated at 100—110°. On heating at 210—230°, it yields a

substance of the composition $(C_3Me_2N_2Ph)_2PtCl_2$ as a yellow powder, insoluble in water. It is sparingly soluble in boiling alcohol, and is precipitated by water from this solution as a flocculent, yellow precipitate.

On boiling 1-phenylpyrazole (2 mol. proportions) with an aqueous solution of sodium platinochloride (1 mol. proportion), sodium chloride and hydrogen chloride are produced, and, on cooling the solution, the substance of the composition $(C_3H_2N_2Ph)_2PtCl_2$, described above, separates out. Under similar conditions 1 : 4 : 5-phenylmethylethylpyrazole and 1 : 4-phenylbromopyrazole yield only resinous products and reduced platinum. 1 : 3 : 5-Phenyldimethylpyrazole, when boiled with an aqueous solution of sodium platinochloride for 7—8 hours, deposits a resinous substance which, on extraction with boiling absolute alcohol and subsequent precipitation with water, yields the compound of the composition $(C_3Me_2N_2Ph)_2PtCl_2$ described above.

The author considers it probable that in these compounds the platinum is directly united with a pentad nitrogen atom in the pyrazole nucleus. W. J. P.

Tetrahydroketoquinoxalines. By M. Georgescu (*Ber.*, **25**, 952—957).—*Phenyltetrahydroketoquinoxaline*, $C_6H_4<\begin{matrix}NH\cdot CHPh\\ |\\ NH\cdot CO\end{matrix}$, is obtained by boiling an aqueous solution of 1 : 2-phenylenediamine and mandelic acid (equal mols.; compare Autenrieth and Hinsberg, this vol., p. 709); it crystallises from dilute alcohol in almost colourless leaflets, melts at 201—202°, and is not attacked by boiling alkali. *Phenyltetrahydroketotoluquinoxaline*, $C_6H_3Me<\begin{matrix}NH\cdot CHPh\\ |\\ NH\cdot CO\end{matrix}$, formed from 1 : 2-diamidotoluene and mandelic acid, melts at 201—202°. A *compound* which may have the constitution $C_6H_4<\begin{matrix}NH\cdot CH\cdot CH_2Ph\\ |\\ NH\cdot CO\end{matrix}$, is produced from 1 : 2-phenylenediamine hydrochloride and phenyl-β-lactic acid; it melts at 216°. The *homologue*

$$C_6H_3Me<\begin{matrix}NH\cdot CH\cdot CH_2Ph\\ |\\ NH\cdot CO\end{matrix}$$

is obtained from 1 : 2-diamidotoluene hydrochloride and mandelic acid; it melts at 240° with decomposition.

Cinnamyltetrahydroketoquinoxaline, $C_6H_4<\begin{matrix}NH\cdot CH\cdot CH:CHPh\\ |\\ NH\cdot CO\end{matrix}$, is obtained by heating 1 : 2-phenylenediamine hydrochloride with phenyl-α-hydroxycrotonic acid in molecular proportion in a sealed tube at 130—140° for 14 hours; it crystallises from alcohol in slightly yellowish needles, melts at 223—224°, and is soluble in hot water, but insoluble in alkalis; the homologous *compound* from 1 : 2-diamidotoluene forms almost colourless crystals, and melts at 185—186°; whilst *cinnamyltetrahydroketonaphthaquinoxaline*, from orthonaphthylenediamine hydrochloride, melts at 174°.

When an alcoholic solution of orthonaphthylenediamine hydro-

chloride and mandelic acid (equal mols., containing a little ammonia is heated in a reflux apparatus on the water-bath for some hours, a *compound*, $C_{10}H_6<\begin{matrix}NH\cdot CHPh \\ NH\cdot C:N\cdot C_{10}H_6\cdot N:C\end{matrix}\!\!\begin{matrix}CHPh\cdot NH \\ ---NH\end{matrix}>C_{10}H_6$, crystallising from aniline in small, brick-red crystals, is obtained; it does not melt at 360°, is insoluble in water, and almost so in alcohol; it forms a pulverulent, dark violet *hydrochloride*. A similar compound, $C_{10}H_6<\begin{matrix}NH\cdot CH\cdot CH_2Ph \\ NH\cdot C=N-C_{10}H_6-N=C\end{matrix}\!\!\begin{matrix}CH_2Ph\cdot CH\cdot NH \\ -NH\end{matrix}>C_{10}H_6$, is formed from orthonaphthylenediamine hydrochloride and phenyl-β-lactic acid.

Methyltetrahydroketotoluquinoxaline, $C_6H_3Me<\begin{matrix}NH\cdot CHMe \\ NH\cdot CO\end{matrix}$, is produced by heating 1 : 2-diamidotoluene hydrochloride and lactic acid in a sealed tube at 130°; it crystallises from boiling water in yellowish leaflets, and melts at 176—177°. *Methyltetrahydroketoquinoxaline*, $C_6H_4<\begin{matrix}NH\cdot CHMe \\ NH\cdot CO\end{matrix}$, obtained from 1 : 2-phenylenediamine hydrochloride and lactic acid, melts at 177°. A. R. L.

Oxazine Dyes. By R. Möhlau (*Ber.*, **25**, 1055—1066). The oxazine dyes may be divided into two groups, which stand in the same relation to one another as the indamines to the indophenols. For the members of the group corresponding with the indamines (gallocyanine, prune, Meldola's blue, muscarine, and Nile blue), the author proposes the collective name *quinoxazine*, as they may be regarded as derivatives of one of the two chromogens which he terms *phenoquinoxazine* (or *quinoxazine*), $\overset{4}{N}H:C_6H_3<\begin{matrix}\overset{1}{N} \\ O\end{matrix}\!\!\begin{matrix} \\ \overset{2}{}\end{matrix}>C_6H_4$, and *naphthaphenoquinoxazine*, $\overset{4}{N}H:C_6H_3<\begin{matrix}\overset{1}{N}\cdot C\cdot C_6H_4 \\ O\cdot CH\cdot CH\end{matrix}\!\!\begin{matrix} \\ \overset{2}{}\end{matrix}>CH$, respectively.

The members of the group corresponding with the indophenols (resorufine, resorufamine, orcirufine, and orcirufamine) may be regarded as derived from the chromogen *phenoquinoxazone* (or *quinoxazone*), $\overset{4}{O}:C_6H_3<\begin{matrix}\overset{1}{N} \\ O\end{matrix}\!\!\begin{matrix} \\ \overset{2}{}\end{matrix}>C_6H_4$, and may collectively be called *quinoxazones*.

Nitrosodimethylmetamidophenol, $C_8H_{10}N_2O_2$ [NOH : O : NMe_2 or NO : OH : NMe_2 = 1 : 2 : 4], prepared by treating dimethylmetamidophenol with hydrochloric acid and sodium nitrite in ice-cold aqueous solution, and then decomposing the product with sodium carbonate (compare D. R.-P. 45268), separates from alcohol in brownish-yellow, moss-like crystals, melts at 169°, and is only sparingly soluble in cold water and ether, but moderately easily in alcohol, and readily in hot water; it gives with alumina, ferric oxide, and chromium sesquioxide coloured lakes, which can be fixed on

vegetable fibres. The *hydrochloride*, $C_8H_{10}N_2O_2,HCl$, crystallises in yellow prisms, and decomposes at 184°; it dissolves in water with partial dissociation, yielding a yellowish-red solution. The corresponding diethyl derivative, $C_{10}H_{14}N_2O_2$, crystallises from alcohol in lustrous, red prisms, melts at 84°, and dissolves freely in hot water, alcohol, and ether; it forms coloured lakes with the oxides of iron, chromium, and aluminium. The *hydrochloride*, $C_{10}H_{14}N_2O_2,HCl$, forms yellow, prismatic crystals, and decomposes at 170°.

Dimethyldiamidoquinoxazone, $^{5}NH_2\cdot C_6H_2{}^{4}O\langle{}^{1}_{O}{}^{N}_{2}\rangle C_6H_3\cdot NMe_2$, is obtained when nitrosodimethylamidophenol is reduced with stannous chloride and hydrochloric acid, the ice-cold solution of the metahydroxyparamidodimethylaniline hydrochloride produced in this way treated with a slight excess of soda, and then air passed through the mixture for several hours; in the last process dimethylamine and ammonia are also formed. The quinoxazone separates from alcohol in yellow, lustrous, rhombic crystals, melts at 223°, and sublimes below its melting point; it is only sparingly soluble in boiling water, yielding a blue solution, but it dissolves moderately easily in alcohol, the reddish-violet solution showing a slight brownish-red fluorescence; it gives with ether, in which it is only sparingly soluble, a rose-red solution which shows a yellowish-red fluorescence, but it is insoluble in alkalis. Its molecular weight was determined in phenol solution, and found to correspond with the molecular formula $C_{14}H_{13}N_3O_2$. In an acetic acid bath it imparts to silk a bluish-violet colour and a brownish-red fluorescence. It has basic properties, and dissolves in excess of dilute mineral acids with an orange-red, in acetic acid with a greenish-blue, and in concentrated sulphuric acid with a bluish-violet coloration, which changes to orange-red on the addition of water. Solutions of the base and of its salts show very characteristic absorption spectra. When the base is treated with reducing agents, it gives a leuco-compound, which is soluble in acids and alkalis, and readily undergoes oxidation.

Dimethylamidoquinoxazone, $C_6H_3{}^{4}O\langle{}^{1}_{O}{}^{N}_{2}\rangle C_6H_3\cdot NMe_2$, can be obtained by diazotising the preceding compound with amyl nitrite in ice-cold alcoholic sulphuric acid solution, and also by heating a mixture of nitrosoresorcinol, dimethylmetamidophenol, and concentrated sulphuric acid on the water-bath until a reaction commences. It separates from benzene in deep-brown, lustrous crystals, and sublimes below 250°, but without melting; it is soluble in alcohol, boiling water, ether, and benzene, the coloured solutions showing a brownish-red or a yellow fluorescence. It dissolves in concentrated sulphuric acid and in hydrochloric acid, yielding blue solutions, which turn red on the addition of water; the mon-acid sulphate crystallises from alcohol in prisms.

Diethyldiamidoquinoxazone, $C_{16}H_{17}N_3O_2$, prepared from nitrosodiethylmetamidophenol as described in the case of the corresponding

dimethyl derivative, separates from alcohol in lustrous, yellow, prismatic crystals, sublimes at 200°, and melts at 211°; it dissolves in boiling water with a violet-blue, in ether with a rose-red, and in alcohol with a reddish-violet coloration; the alcoholic solution shows a brownish-red and the ethereal solution a yellowish-red fluorescence. It gives with acetic acid blue, with concentrated sulphuric acid violet, and with excess of dilute mineral acids brownish-red solutions; its tinctorial action on silk in an acetic acid bath is similar to that of the dimethyl derivative. F. S. K.

The so-called Dinitrosoazobenzene. By F. Kehrmann and J. Messinger (*Ber.*, **25**, 898—901).—The authors find that the compound described as dinitrosoazobenzene by Willgerodt and Ferko (Abstr., 1888, 829) is in reality nitrophenylazimidobenzene (meso-phenylphentriazole; see next abstract), $\overset{4}{NO_2}\cdot C_6H_3\ll\overset{1}{N}\underset{2}{N}>NPh$; it is prepared by boiling together in a reflux apparatus bromodinitrobenzene [Br : $(NO_2)_2$ = 1 : 2 : 4] (20 grams), phenylhydrazine (2 mols.), sodium acetate (1 mol.), and alcohol (200 c.c.). The corresponding amido-derivative is obtained when the nitro-compound is boiled in a reflux apparatus with the necessary quantity of stannous chloride, an excess of hydrochloric acid, and alcohol for an hour; it crystallises from alcohol in lustrous, yellow, concentric groups of flat needles, melts at 183°, and is almost insoluble in water. The aqueous solution exhibits a green, the alcoholic a bluish-green, and the ethereal a blue fluorescence; whilst the solutions in benzene and chloroform fluoresce violet. When the base is dissolved in concentrated sulphuric acid, and the cooled solution treated with the calculated quantity of sodium nitrite solution, Gattermann and Wichmann's compound melting at 109° (Abstr., 1888, 829) is formed. A. R. L.

Nomenclature of Rings consisting of 2 Carbon and 3 Nitrogen Atoms. By F. Kehrmann and J. Messinger (*Ber.*, **25**, 901—903).—The authors adopt Widmann's nomenclature. The compounds $NH<\begin{matrix}N:CH\\|\\N:CH\end{matrix}$ and $N\ll\begin{matrix}NH\cdot CH\\||\\N-CH\end{matrix}$ are named orthotriazole and isorthotriazole respectively; whilst the substitution derivatives of these are distinguished by prefixing *N* or C, according as the substitution takes place in the NH or CH groups; in the former case, they may also be designated meso-derivatives. The complex

$$C_6H_4\ll\overset{N}{N}>NH$$

is named phentriazole. The same principle is used in the case of metatriazole, $NH<\begin{matrix}CH:N\\|\\CH\cdot N\end{matrix}$, and isometatriazole, $N\ll\begin{matrix}CH\cdot NH\\|\\CH:N\end{matrix}$. The dihydro- and tetrahydro-triazoles may be called triazolines and triazolidines respectively. A. R. L.

A Substance which contains a Ring of 18 Members, and gives an Abnormal Freezing-point Depression. By E. Lellman and B. Arnold (*Ber.*, **25**, 662—664).—The substance, melting at 231°, obtained by reducing orthodinitrodibenzylamine with stannous chloride in alkaline solution or with zinc-dust and soda in alcoholic solution, to which the constitution $HN<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$ was assigned (this vol., p. 316), gives no constant molecular depression of the freezing point, whatever solvent be used; the numbers obtained corresponded with molecular weights varying from 186 to 672. By determining the lowering of the boiling point, however, of a solution in phenol, a constant molecular weight of 437 was obtained. The formula of the substance must thus be doubled, giving a molecular weight of 446. A further argument for this is the fact that the substance $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$, obtained by reducing orthodinitrobenzylparatoluidine, melts at 211°. Hence, if the constitution at first assumed for the substance in question is correct; a replacement of hydrogen by tolyl has been attended by a lowering of the melting point from 231° to 211°, an unlikely occurrence. The formula must then be doubled and written $HN<\begin{matrix}CH_2\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot CH_2\\ CH_2\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot CH_2\end{matrix}>NH$. It contains a ring of 12 carbon and 6 nitrogen atoms, and may be termed *di-orthoazodibenzylamine*. Perhaps there is a connection between the size of this ring and the abnormal molecular depression.

C. F. B.

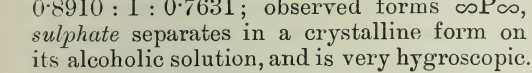
Adenine. By M. Krüger (*Zeit. physiol. Chem.*, **16**, 329—339: compare this vol., p. 219).—On decomposition, adenine, hypoxanthine, xanthine, and uric acid yield glycocine, carbonic anhydride, and formic acid; the relation between the amounts of the two last-named products depending on the amount of oxygen they contain. Adenine and hypoxanthine, moreover, both contain a radicle adenyl. On account of the close relationship between these substances, it appeared advisable to investigate the question whether adenine and hypoxanthine resemble uric acid and xanthine in containing an alloxan nucleus.

On treating adenine with bromine, a dark-red substance is formed which is bromadenine-tetrabromide-hydrobromide (Bruhns and Kossel, this vol., p. 220); under certain circumstances, however, this compound holds excess of bromine, which is evolved on the application of heat. Bromadenine is prepared from the compound so purified by dissolving it in warm sodium hydroxide and then passing a stream of carbonic anhydride through the solution. Bromadenine is by this means precipitated. Dry chlorine has no action on dry bromadenine; if, however, water is added, bromine is evolved. The oxidation products obtained from bromadenine by means of hydrochloric acid and potassium chlorate are alloxan, urea, oxalic acid, and another acid of undetermined constitution. In other words, this method of research shows the existence of an alloxan nucleus in

adenine; the oxalic acid is doubtless derived from the alloxan, and the urea probably from a urea nucleus which adenine also contains.

W. D. H.

ψ-Tropine and some ψ-Tropeïnes. By C. Liebermann and L. Limpach (*Ber.*, **25**, 927—939; compare Abstr., 1891, 1265).—By the spontaneous evaporation of its solution in benzene, ψ-tropine is obtained in large crystals belonging to the rhombic system, $a : b : c = 0{\cdot}8910 : 1 : 0{\cdot}7631$; observed forms $\infty\breve{P}\infty$, ∞P, P, and $\breve{P}\infty$. The *sulphate* separates in a crystalline form on the addition of ether to its alcoholic solution, and is very hygroscopic. The relation of tropine to ψ-tropine is thus shown :—



ψ-Tropine is converted into tropidine by the method described by Ladenburg for the conversion of tropine into the latter (Abstr., 1883, 670); tropidine platinochloride was obtained in crystals having the form observed by Bodewig (*Zeit. Kryst. Min.*, **5**, 566).

Mandelic ψ-tropeïne (*ψ-homatropine*), $C_8H_{14}NO{\cdot}CO{\cdot}CHPh{\cdot}OH$, is best prepared by a method similar to that devised by Ladenburg for the synthesis of atropine, thus :—A solution containing equivalent weights of ψ-tropine and mandelic acid is continually evaporated for four successive days, dilute hydrochloric acid (1 : 40) being added at intervals; it is a viscid oil, and both the *sulphate* and *hydrochloride* are very hygroscopic; the *platinochloride* is a yellowish precipitate which readily resinifies, and the *aurochloride* is a yellow precipitate. An acid solution of the base gives with potassium mercuric iodide a white, resinous precipitate, and with picric acid a yellow precipitate. The base yields mandelic acid and ψ-tropine when heated at 60° with barium hydroxide solution, and it is decomposed in the cold by an excess of mineral acids; a solution of the acetate is devoid of mydriatic properties.

Tropyl-ψ-tropeïne (*ψ-atropine*), $C_8H_{14}NO{\cdot}C_9H_9O_2$, is prepared, similarly to the last-described base, from ψ-tropine and tropic acid; it is a white, viscid oil, having a specific rotatory power in alcoholic solution $[\alpha]_D = -4{\cdot}9$; when it is dissolved in benzene, and petroleum added to the solution until it is turbid, white, nodular crystals separate after some weeks; these melt at 86—88°. The *hydrochloride* forms white, hygroscopic needles, and melts at 183° with decomposition; the *aurochloride* forms yellow needles, and melts at 198°. A moderately dilute solution of the base gives a bright-yellow, flocculent precipitate with platinic chloride, and it exhibits no mydriatic properties. It therefore differs from hyoscine, which, according to Ladenburg (Abstr., 1881, 56), is ψ-atropine; like the latter, however, it is hydrolysed by barium hydroxide solution with the formation of tropic acid and ψ-tropine. Although the difference between these two compounds is not yet ascertained, it is suggested that their relation may be similar to that of hyoscyamine to atropine. In the above synthesis of tropyl-ψ-tropeïne, about 50 per cent. of the tropic acid employed was converted into tropide; the authors have re-established the empirical formula given by Ladenburg for this com-

pound, but find that its molecular formula is twice this. When a solution of tropide and ψ-tropine in benzene is heated in a sealed tube at 120°, *ψ-tropine atropate*, $C_8H_{15}NO,C_9H_8O_2$, a compound soluble in water and melting at 129°, is produced; this was also prepared by way of control from tropine and atropic acid. The authors confirm Ladenburg's observation, that when tropide is heated at 60° with barium hydroxide solution, about four-fifths is converted into tropic acid; and they find that the remainder is transformed into atropic acid. The constitution of tropide is probably represented by the formula $CHPh<\begin{matrix}CH_2\cdot O\cdot CH_2\\CO-O-CO\end{matrix}>CHPh$. Tropyl-ψ-tropeïne (see above) can be obtained by heating ψ-tropine with tropide at 200°.

A. R. L.

Conversion of Cupreïne into Quinine. By E. Grimaux and A. Arnaud (*Annalen*, **267**, 379—380).—A reply to Hesse (*Annalen*, **266**, 240; this vol., p. 221); the authors maintain the correctness of the experiments which were criticised by Hesse, and claim to have been the first to accomplish the conversion of cupreïne into quinine, and also to prepare quinine dimethiodide (see further, *Compt. rend.*, **114**, 548). F. S. K.

Cinchonine. By M. Freund and W. Rosenstein (*Ber.*, **25**, 880—882).—The authors are continuing the work of Claus and Müller on the halogen alkyl compounds of cinchonine and the products obtained by treating them with potash.

Dimethylcinchonine, $C_{19}H_{20}Me_2N_2O$, is obtained by extracting with ether the product of the action of strong potassium hydroxide on an aqueous solution of methylcinchonine methiodide. It is a yellow oil, insoluble in water, and yields well-characterised salts. The *hydrochloride* crystallises in white plates, and melts at 124—125°. The *hydrobromide* is somewhat less soluble than the hydrochloride, and melts at 111°. The *hydriodide* melts at 74°. The *methiodide*, $C_{19}H_{20}Me_2N_2O,MeI$, is a well-crystallised compound, and melts at 175—177°. E. C. R.

Alkaloïds of Lupinus albus. By A. Soldaini (*Gazzetta*, **22**, i, 177—180).—The concentrated aqueous extract obtained from *Lupinus albus* is mixed with caustic lime and extracted with petroleum in a reflux apparatus. The solution yields two isomeric alkaloïds, the one being a solid substance crystallising in monosymmetric prisms, $a : b : c = 1{\cdot}7983 : 1 : 1{\cdot}6710$; $\beta = 83°\ 14'$, melting at 99°, and the other a viscous liquid. The solid alkaloïd is found by analysis and cryoscopic determinations to have the composition $C_{15}H_{24}N_2O$. Its *hydrochloride*, $C_{15}H_{24}N_2O,HCl + 2H_2O$, melts at (?) 124—135°. The *hydriodide*, $C_{15}H_{24}N_2O,HI$, melts at 185°. The *methiodide*, $C_{15}H_{24}N_2O,MeI$, melts at 233°, and the *bromide*, $C_{15}H_{24}N_2O,Br_3$, at 124—125°. The *platinochloride*, $(C_{15}H_{24}N_2O)_2,H_2PtCl_6$, the *aurochloride*, $C_{15}H_{24}N_2O,HAuCl_4$, and the *thiocyanate*, $C_{15}H_{24}N_2O,HSCN + H_2O$, which melts at 124°, have also been prepared. The liquid alkaloïd seems to be identical with the lupanine extracted from *Lupinus*

angustiflora by Hagen (Abstr., 1886, 163) and Siebert (Abstr., 1892, 223). W. J. P.

Ephedrine from Ephedra monostachia. By P. Spehr (*J. Pharm.*, **25**, 403—404; from *Pharm. Zeit. Russ.*, **31**, 1).—To obtain the alkaloïd, the coarsely-pulverised plant and root is extracted with alcohol of 80° Tr.; the alcohol is removed, sodium carbonate is added, and the liquid shaken with ether; the crude alkaloïd remaining on expelling the ether is then transformed into hydrochloride and purified by repeated crystallisation. The alkaloïd thus obtained, *ephedrine*, is not the only one which has received this name. Nagaï, of Tokio, extracted an alkaloïd from *Ephedra vulgaris* var. *helvetica*, to which he gave this name; and the commercial firm of Merck, of Darmstadt, has extracted from the same genus an alkaloïd named *pseudoephedrine*. To avoid confusion, the distinctive characters of these forms are given in the following table :—

	Nagaï's Ephedrine.	Pseudo-ephedrine.	Spehr's Ephedrine.
Formula	$C_{10}H_{15}NO$	$C_{10}H_{15}NO$	$C_{13}H_{19}NO$
Melting point of the base	210°	115°	112°
Melting point „ hydrochloride	216°	174°	207°
Solubility in water	scarcely soluble	1 : 454	very soluble
Solubility in alcohol	easily „	very soluble	„ „
Solubility in absolute ether	„ „	1 : 15	1 : 98
Solubility in benzene	„ „	1 : 26	1 : 1180
Solubility in chloroform	„ „	1 : 8	1 : 11
Taste	bitter	bitter	burning
Physiological action	very poisonous and mydriatic	very poisonous and mydriatic	very feeble
Crystalline form of the base	rhombic	rhombic	monoclinic
Crystalline form „ hydrochloride	„	„	hexagonal

J. T.

Glaucine. By J. A. Battandier (*J. Pharm.*, **25**, 350—351).—It is impossible to obtain pure crystallised salts by Probst's method. Brilliant, needle-shaped crystals of hydrobromide can be obtained by the following process :—The concentrated sap of the leaves of *Glaucium luteum* is extracted with ammonia and light petroleum. The petroleum is treated with water, acidified with acetic acid, and glaucine acetate is precipitated by ammonia as a white, curdy mass. Glaucine thus thrown down gradually darkens in colour even when protected from light. On dissolving it in 95 per cent. alcohol, and saturating the solution with aqueous hydrobrombic acid, glaucine hydrobromide immediately crystallises out, leaving the brown alteration products still dissolved in the alcohol. These crystals washed with a little strong alcohol, and recrystallised from boiling alcohol, yield beautiful, prismatic needles. The hydrobromide is much more soluble in water than in alcohol. Glaucine, or its salts, treated with concentrated sulphuric acid, gives a beautiful, sky-blue colour, which

only on heating, or after some days in the cold, becomes violet. The brown alteration products of glaucine give up to light petroleum a white alkaloïd resembling glaucine, but which affords an immediate violet colour with sulphuric acid. Recently prepared glaucine yields a colourless hydrobromide, but the mother liquors soon give crystals of a rosy tint, which are only decolorised with difficulty by animal black. A beautiful reaction for glaucine is the following:—4 drops of acid mercuric nitrate is added to 10 c.c. of sulphuric acid and stirred up; a porcelain saucer is smeared with this mixture, and minute crystals of glaucine, or one of its salts, are dropped on to the smears. On inclining the saucers, intense green striæ are formed which gradually become red. J. T.

Aristolochia argentina. By O. Hesse (*Pharm. J. Trans.* [3], **51**, 551).—The root of *Aristolochia argentina* is treated with ether and then with alcohol; on evaporation, the alcoholic extract yields a resinous mass partly soluble in solution of sodium hydroxide, and giving up to ether a base, for which the author proposes the name *aristine*. This base dissolves in hot glacial acetic acid, and, on cooling, crystallises out in gold-coloured laminæ and needles. It is sparingly soluble in hot alcohol, but more soluble in ether, chloroform, and benzene. It decomposes when heated to 260°. Concentrated sulphuric acid turns the acetic anhydride solution first blue, then greenish-blue. Its alcoholic solution is neutral, but forms red compounds with ammonia and with soda. The author mentions another base from the same source, which base he would call *aristolochine*, although the name has already been applied by Chevallier to a substance obtained from *Aristolochia serpentaria*. *Aristolochine* is precipitated from its acid solutions by caustic alkalis, and is soluble in alcohol, ether, chloroform, and benzene, which, on evaporation, leave it as a colourless, resinous mass. R. R.

"Pillijan": Lycopodium saururus. By P. N. Arata and F. Canzoneri (*Gazzetta*, **22**, i, 146—157).—This plant occurs in South America, and contains an alkaloïd named pillijanine, which has previously only been obtained in an impure state. The authors extract it in the following manner:—A quantity of the fresh plant (25 kilos.) is bruised and boiled with a large quantity of water acidified with tartaric acid. The liquid is filtered and partially evaporated on the water-bath, calcium hydroxide added, and the whole evaporated to dryness. The residue is then extracted with boiling alcohol for three days in a reflux apparatus, light petroleum and amyl alcohol being subsequently used to complete the extraction. The liquids used for extraction are mixed and distilled; the residue is dissolved in dilute acetic acid, filtered, and the solution treated with lead acetate, and again filtered. The lead is separated from the filtrate by hydrogen sulphide, and on evaporating the solution, a syrup is obtained, which is dissolved in water and extracted with ether. The aqueous solution is saturated with sodium carbonate and extracted with chloroform. On evaporating the chloroform solution the alkaloïd (15—20 grams) is obtained as a reddish mass, possessing

a powerful odour resembling that of coniine. It is further purified by precipitating the aqueous solution of its sulphate with caustic alkali, and extracting with light petroleum. The alkaloïd crystallises from the petroleum solution in needles melting at 64—65°, and has the composition $C_{15}H_{24}N_2O$. Solutions of its salts give yellowish precipitates with auric chloride, potassium dichromate, iodine solution, and bromine-water. Ferric chloride, potassium ferricyanide, and tannin solutions give reddish, green, and whitish precipitates respectively. The *sulphate*, $(C_{15}H_{24}N_2O)_2,H_2SO_4 + 2\frac{1}{2}H_2O$, forms large, deliquescent crystals. The *hydrochloride* crystallises with difficulty in small tablets, and is very deliquescent. The *platinochloride* crystallises in yellow laminæ, is very soluble in water and alcohol, and decomposes at 200° without melting. The *aurochloride* forms splendid, yellow crystals, very rapidly altered by light. On distilling pillijanine in a current of hydrogen, a volatile base having the properties of nicotine is obtained; the alkaloïd is hence very possibly amyloxynicotine, $C_{10}H_{13}N_2{\cdot}OC_5H_{11}$. It acts as a powerful poison. A dose of 0·1—0·2 gram of the hydrochloride administered to a dog causes convulsions, violent vomiting, contraction of the pupil of the eye, and finally death. W. J. P.

Peptone Salts from Glutin. By C. Paal (*Ber.*, **25**, 1202—1236). —Mineral acids act on glutin in a similar manner to pepsin and trypsin, yielding peptones, which combine with the acid present to form salts; these dissolve not only in water, but also, unlike the free peptones, in absolute ethyl and methyl alcohol. For their preparation, 100 parts of purest commercial gelatin are warmed on the water-bath with 160 parts of water and 40 parts of concentrated hydrochloric acid until a portion of the product is completely soluble in a large quantity of absolute alcohol, and the whole is then poured into 4—5 vols. of absolute alcohol. After filtering off the inorganic salts, the solution is precipitated with ether, the residue redissolved in alcohol, and the solution evaporated under diminished pressure. The glutin peptone hydrochloride thus obtained forms a brittle, white, vesicular mass, and is readily soluble in water, methyl alcohol, ethyl alcohol, and acetic acid, somewhat less easily in propyl alcohol, sparingly in amyl alcohol, and insoluble in ether, carbon bisulphide, and benzene. It is very hygroscopic, remains unchanged at 130°, and gives the characteristic peptone reaction with biuret; it is lævorotatory in aqueous solution, $[\alpha]_D$ being about −60°. The quantity of hydrochloric acid found in the different preparations varied from 10·5—12·5 per cent., whilst the ash is only about 0·5 per cent. If stronger hydrochloric acid than that mentioned above is employed, or if the heating be continued for a longer time, salts containing a larger percentage of acid can be obtained.

The quantity of carbon and hydrogen varies considerably in the different preparations, the former being in some cases higher than that of glutin (for which the author finds C = 50·1, H = 6·68), and in others less; this is due to the fact that in most cases more or less etherification has taken place during the treatment with alcohol; the compounds formed may, however, be hydrolysed by long-continued

boiling with water. The salts were found to be almost free from sulphur.

The fact that by varying the strength of the hydrochloric acid, and the time allowed for the reaction, compounds containing a varying amount of acid are obtained, tends to show that these salts are a mixture of compounds representing different degrees of peptonisation; this has been confirmed by subjecting the alcoholic solutions to fractional precipitation with ether, and subsequent fractional crystallisation of some of the precipitates from alcohol. The salts thus obtained contain a varying percentage of acid, their solubility in alcohol decreasing with the decrease in the proportion of acid. A much more satisfactory separation is obtained by subjecting an aqueous solution of the salts to dialysis, for although they have not been obtained crystalline (probably owing to their hygroscopic nature), they, nevertheless, pass through the dialyser, and must be regarded as crystalloïds. In this manner, a salt containing 10·56 per cent. of acid was separated into two portions, that passing through the dialyser containing 14·19 per cent. of acid, and the residue only 5·79, the latter being insoluble in absolute alcohol. The percentage of carbon and hydrogen, calculated on free peptone, remains fairly constant, except in so far as the salts passing through the dialyser are concerned; the decrease in this case is due to the fact that in evaporating the large volume of solution obtained, a quantity of alcohol is split off. It was found that only those salts containing 10 per cent. of acid and upward are soluble in absolute alcohol, and those fractions which are only just dissolved are much less soluble in propyl alcohol, and insoluble in amyl alcohol; the salts containing less than 10 per cent. are all readily soluble in methyl alcohol, and these also dissolve in alcoholic solution of the salts containing more acid.

The same separation may be brought about by treating the alcoholic solution of the salt with mercuric chloride: two mercurochlorides are thus obtained, one of which separates out at once, and the second on the addition of ether; these correspond to the insoluble and soluble hydrochlorides, and may, like the mercurochlorides of the free peptones, be employed for therapeutical purposes.

If glutin be warmed with a weaker acid than that first mentioned, a salt may be obtained which dissolves in methyl alcohol, but is insoluble in ethyl alcohol, and contains 6·85 per cent. of hydrochloric acid. It closely resembles the salts already described, and may, like them, be separated into fractions containing different percentages of acid, that containing the highest percentage being somewhat soluble in ethyl alcohol. By the action of pepsin on glutin in presence of very dilute hydrochloric acid, a peptone salt is also obtained which closely resembles the salt last described, but is not completely soluble in cold methyl alcohol; it is separated by dialysis into two fractions, one of which contains 2·97 per cent. HCl, and is almost insoluble in methyl alcohol, whilst the other contains 11·13 per cent. HCl.

In all cases it appears that the salts formed either by the action of

acid or of pepsin and acid are separable into two portions containing a maximum and minimum percentage of acid, and it therefore appears probable that the molecule of glutin contains two atom-complexes, which in the first stage of the reaction yield two separate molecules. These differ greatly in the resistance they offer towards further change, the one which forms salts containing a larger quantity of acid, being more readily converted into its ultimate products of decomposition, namely, the amido-acids.

The acid in the glutinpeptone salts is very firmly combined, and great difficulty was experienced in converting the salts into the free peptones. This was first accomplished by adding a large excess of alkali and removing the inorganic substances by dialysis, but great loss of substance also takes place. It was then found that the change may be brought about quantitatively by adding a slight excess of pure silver sulphate, filtering from silver chloride, removing the excess of silver with hydrogen sulphide, and the sulphuric acid with the necessary amount of baryta-water. The glutinpeptones thus obtained are soluble in all proportions in water, but insoluble in alcohol and ether; their aqueous solutions have an acid reaction towards litmus, but do not turn Congo paper blue. On analysis, it was found that the percentage of carbon was rather less, and that of hydrogen rather more, than in the case of glutin; this is in complete agreement with the supposition that they are products of hydrolysis.

Attempts were also made to determine the molecular weights of these substances by the cryoscopic method in aqueous solution and by the boiling-point method in aqueous and methyl and ethyl alcoholic solution. The results show that the molecule of peptone salt becomes smaller as the percentage of acid increases; further, that the salts are dissociated in aqueous and methyl alcoholic solutions, but not in ethyl alcoholic solution, for the molecular weight deduced from the boiling point of the solutions in the last solvent is double that deduced in the same manner from the boiling point of the solutions of the same salt in the other two solvents. In water and methyl alcohol, the molecule of the salt is therefore dissociated into 2 mols., whence it follows that these salts consist of 1 mol. of peptone and 1 mol. of hydrochloric acid. The molecular weight of the free peptones was found to be about 300 in three cases, and about 215 in a fourth case, and that of glutin itself about 900.

The author concludes that the glutin molecule is resolved with assimilation of water into peptone molecules of gradually decreasing molecular weight, till a point is reached at which the peptonisation ceases, and the simpler peptones are resolved into amido-acids, lysin, lysatin, &c. As, however, the molecule of the proteïds consists of two atom-complexes which present a varying resistance to further hydrolysis, the simpler products of decomposition are always mixed with unaltered peptones. H. G. C.

Solubility of Fibrin. By C. Fermi (*Zeit. Biol.*, **28**, 229—236). —The dissolution of fibrin and its change into peptone are the two criteria by means of which the presence of a proteolytic ferment is ascertained. But in those cases in which the ferments are weak the

change into peptone is difficult to make out, and the solution of the fibrin remains the only test. It is thus important to know how far fibrin is soluble in acids, saline solutions, and so forth when no proteolysis occurs, and the difficulties are increased by the fact that fibrin prepared from arterial blood is more difficult of solution than that from venous blood (Denis, *Physiol. der Sang*, Paris, 1838, 1856, 1859; Scherer, *Ann. Chem. Pharm.*, **40**, 18; Zimmerman, *Roser and Wunderlich's Archiv physiol. Heilk.*, **5**, 349; **6**, 53); moreover, the fibrin differs in different animals (Scherer, Zimmerman, Deutschmann, *Pflüger's Archiv*, **10**, 501).

The following are the results of the present investigation :—

1. Pig's fibrin dissolves in 5 per 1000 hydrochloric acid in a few hours, ox fibrin requires several days. Pig's fibrin does not dissolve much more quickly if pepsin is added.

2. The same is true for other acids (malic, formic, oxalic, butyric, acetic, citric, lactic, nitric, sulphuric). Pig's fibrin always dissolves most easily, ox fibrin least easily; the fibrins of the sheep and horse are intermediate.

3. Hydrochloric acid is the most powerful; nitric, sulphuric, acetic, and butyric acids the least.

4. Warmth accelerates the solution.

5. Boiled fibrin is very difficult of solution.

6. The dissolved fibrin is a proteïd which is precipitated by neutralisation.

7. Fibrin does not appear to contain within itself a fibrin-dissolving ferment.

It thus is seen that the mere solution of the fibrin is no trustworthy test for a proteolytic enzyme. If, however, there is no other available, due attention must be paid to the source of the fibrin, the strength of the acid used, and the time taken for solution; a large number of control tests must be employed. W. D. H.

Hæmocyanin. By A. B. Griffiths (*Compt. rend.*, **114**, 496).—Blood of *Homarus*, *Sepia*, or *Cancer* is precipitated by magnesium sulphate, and the precipitate dissolved in water, reprecipitated by alcohol, purified, and dried at 60°, and finally in a vacuum. The analyses of specimens thus prepared from different sources agree well, and lead to the empirical formula $C_{867}H_{1363}N_{223}CuS_4O_{258}$. Hæmocyanin is more stable than hæmoglobin. Jn. W.

Blue Colouring Matter in the Blood of Crustaceæ. By F. Heim (*Compt. rend.*, **114**, 771—774).—Hæmocyanin, the blue colouring matter formed by the action of air on the almost colourless blood of the Crustaceæ, is usually described as a proteïd analogous in properties and function to the hæmoglobin of the Vertebrata. It is also said to contain copper as an essential constituent, and to be the only proteïd in the blood of Crustaceæ.

The author confirms the statement that it exists in two states, reduced and colourless, oxidised and coloured. The combination with oxygen is destroyed by exposure in a vacuum, passage of an inert gas, action of reducing agents, &c.

Contrary to the usual statement, the author finds that the blood of the Crustaceæ contains serum identical in its properties with that of the Vertebrata, and paraglobulin derived from the serum. Dialysis consequently yields a mixture of hæmocyanin with a large quantity of serum, and not pure hæmocyanin.

Copper is not an essential constituent of hæmocyanin; although present in the lobster, it does not occur in the crab, hermit crab, crayfish, sea crayfish, and about half the Crustaceæ.

Direct estimation shows that the quantity of available oxygen present in hæmocyanin is not greater than that present in water.

Attempts to isolate pure hæmocyanin were not successful, and it is doubtful whether it is really a proteïd. It differs essentially from hæmoglobin in the absence of a metal as a necessary constituent of its molecule and in its feeble absorption coefficient for oxygen; it does not crystallise, does not combine with carbonic oxide, and does not resist putrefaction. The so-called hæmocyanin observed by Fredericq in the putrefied blood is blackish, and not blue, and has none of the properties of hæmocyanin. It is analogous to melanin, and is formed also in the putrefaction of hepatic tissue. C. H. B.

Physiological Chemistry.

Unorganised Ferments. By G. Tammann (*Zeit. physiol. Chem.*, **16**, 271—328).—Whereas mineral acids further all hydrolyses, the enzymes only act on particular materials, some producing hydrolysis of starch, others of proteïds, and so forth. The hydrolysis produced by acids is complete; that produced by enzymes (with certain exceptions—invertin, rennet) is usually incomplete, especially if the quantity of material to be acted on is large. This is due to the fact that during its activity the ferment is converted into an inactive modification, and the transformation usually occurs before the ferment reaction is completed. This change is brought about by the products of the ferment action; removal or dilution of these products, or elevation of temperature, allows the ferment action to continue, as by these means the inactive is reconverted into the active modification. Too high a temperature, however, changes the ferment in such a way that it is not possible to obtain from it again the active modification. W. D. H.

Unorganised Ferments. By J. Jacobson (*Zeit. physiol. Chem.*, **16**, 340—369).—Soluble ferments, in addition to their specific action, have in common the power of liberating oxygen from hydrogen peroxide. The ferments specially investigated in the present research were emulsin, diastase, and pancreatin. The influence of elevated temperature in destroying the activities of the ferments differentiates their two actions; at a certain temperature (differing

in different ferments, and according to whether they are in a dry or dissolved condition), the power to decompose hydrogen peroxide is lost; the specific action of the ferment is usually weakened at this temperature, but it is not destroyed until a higher temperature is applied.

Alkali up to 0·12 per cent. augments the oxygen-liberating activity of the ferments; a percentage of 0·25 destroys it. Hydrochloric acid of a strength of 0·008 per cent. lessens, and of 0·035 destroys, this activity.

The influence of a very large number of inorganic and organic compounds in this direction was also tried; and the results are given in detail. There appears, however, to be no general conclusion to be drawn from these experiments: some hinder, some accelerate, and others have little or no influence; it is not possible to class these according to their chemical constitution. W. D. H.

Glycolysis in Blood. By M. Arthus (*Compt. rend.*, **114**, 605—608).—Glycolysis in blood is a phenomenon of chemical fermentation and is not due to the development of microorganisms; it takes place in blood collected aseptically in sterilised vessels. The presence of actually living elements in the blood is not necessary, for the destruction of the sugar takes place in serum or oxalated plasma free from globules, in blood diluted with several volumes of water, and in blood which, after being kept for 24 hours at 15°, is mixed with 1 per cent. of sodium fluoride. The glycolytic ferment does not preexist in living blood, but is formed outside the blood vessels at the expense of the elements of the envelopes of the white corpuscles. Its formation seems to be a consequence of the extravascular life of these corpuscles. Fresh blood shows very little glycolytic power, but this power gradually develops when the blood is kept. Addition of sodium fluoride to freshly drawn blood prevents the development of the glycolytic ferment, but does not prevent its destructive action on sugar if time has been given for the development of the ferment before the addition of the fluoride. Sodium oxalate has a similar effect. The action of the ferment is very feeble at 0°, but becomes more energetic as the temperature rises, and is strongly marked at 40° to 50°; at 55°, the ferment is destroyed. It will be seen that the glycolytic ferment behaves in many ways similarly to the fibrin ferment: glycolysis will continue for several days at 10° in defibrinated aseptic blood, and for several weeks in aseptic oxalated blood. Direct experiment shows that the apparent absence of glycolysis when the blood is first drawn is not due to a compensating development of sugar from glycogen or other substances; it is due to the fact that the glycolytic ferment does not preexist in the blood, but is formed after the latter is removed from the blood vessels. C. H. B.

Fermentation of Blood. By Berthelot and G. André (*Compt. rend.*, **114**, 514—520).—The experiments were made with defibrinated bullock's blood of sp. gr. 1·045 at 15°, and fermentation was allowed to continue for 130 days, at first at a temperature of 35°, and towards the end at 45°. The products under these conditions are carbonic

anhydride, ammonia, traces of hydrogen sulphide, volatile fatty acids, and non-volatile nitrogenous compounds. The liquid retains the reddish-brown tint of altered blood. The following table shows the composition of 1000 c.c. of the original defibrinated blood, exclusive of inorganic salts and water, together with the composition of the products :—

	C.	H.	N.	O.	Total.
					grams.
Original blood	87·0	11·8	26·0	37·6	162·4
Carbonic anhydride	7·3	—	—	20·0	27·3
Ammonia	—	3·6	16·7	—	20·3
Volatile fatty acids	26·5	4·4	—	21·1	52·0
Non-volatile nitrogen compounds.	53·0	8·0	9·7	32·4	103·1

Of the total quantity of carbonic anhydride formed, 22·5 grams is evolved in the gaseous state, whilst 4·8 grams remains in combination in the liquid. It is especially noteworthy that the gas evolved is quite free from hydrogen and nitrogen. In the case of the ammonia, 3·6 grams remains in the liquid in the form of compounds decomposable by magnesium oxide, whilst the rest is either evolved during fermentation, or can be expelled by a current of hydrogen.

The carbonic anhydride and ammonia are formed in practically equivalent proportions, as in the fermentation of urea, but in the case of blood they are derived from proteïds which are analogous to ureïdes in their mode of decomposition. Two-thirds of the total quantity of nitrogen is converted into ammonia, and hence it would seem that two-thirds of the proteïds decompose after the manner of ureïdes.

The volatile fatty acids include all members of the acetic series from formic to caproic acid, and even beyond, but their mean composition lies between that of propionic and butyric acids, the extremes of the series being present in comparatively small quantity. These products are similar to those resulting from butyric fermentation, with the essential difference that no hydrogen is evolved during the change.

The non-volatile nitrogen compounds are :—(1.) An insoluble, brown compound of a humoid character; it has the empirical composition $C_{18}H_{24}N_2O_3$, and is a condensed anhydride. (2.) Nitrogenous acids forming crystallisable barium salts, the first crop having the composition $C_{55}H_{105}Ba_2N_9O_{22}$, and the second $C_{31}H_{56}BaN_6O_{16}$. (3.) A non-crystallisable compound soluble in alcohol; it has the composition $C_{18}H_{33}N_3O_{10}$ or $C_6H_{11}NO_3$. (4.) Compounds insoluble in alcohol but forming salts partially crystallisable from water; they are formed in small quantity, but seem to be amido-acids related to the fatty series, the salts having the mean empirical formula $C_{12}H_{24}N_2O_3 + n\mathrm{RO}$. The composition of the nitrogen compounds formed from 1000 c.c. of blood is summarised in the following table :—

	C.	H.	N.	O.
Brown, insoluble substance	4·62	0·50	0·56	1·06
Nitrogenous acids	18·88	3·02	3·66	11·12
Compounds soluble in alcohol	25·76	4·08	5·00	19·02
Compounds insoluble in alcohol	2·86	0·46	0·52	1·24
	51·92	8·03	9·74	32·44

No volatile nitrogenous bases are formed, nor any alcohol or acetone; but traces of a pungent compound, probably a thioaldehyde, and of a volatile substance with a camphoraceous odour were observed.

It will be noticed that whilst the total weight of the carbon compounds in 1000 c.c. of blood was 162·4 grams, the total weight of the products was 202·7 grams. The increase of 40·3 grams is due solely to oxygen and hydrogen, which, moreover, have been assimilated in the proportions in which they exist in water. Further, two molecules of water have been assimilated for each molecule of ammonia formed; this ratio is characteristic of the nitriles. On the other hand, the formation of ammonia and carbonic anhydride in equivalent proportions, a relation characteristic of the ureïdes, would indicate the assimilation of one molecule of water for each atom of nitrogen. The ureïdes, however, require the assimilation of a molecule of water before decomposing by further hydrolysis in the manner of urea. One-third of the total nitrogen remains in solution in the form of stable nitrogen compounds.

It is noteworthy that one-twelfth of the carbon is evolved in the form of carbonic anhydride, and one-third of the remainder is converted into fatty acids, and two-thirds into amido-compounds.

The comparative simplicity of these relations is of considerable interest. C. H. B.

Formation of Glycogen from different Sugars. By C. Voit, J. G. Otto, A. C. Abbott, G. Lusk, and F. Voit (*Zeit. Biol.*, **28**, 245—292).—From the examination of previous and the present researches on glycogen formation in the liver, it is believed that glycogen may originate in two ways: first, it is a temporary store of carbohydrate food, and, secondly, it may be the result of proteïd metabolism. The present research was performed on animals (rabbits, hens) in which the hepatic glycogen had been reduced to a minimum by starvation, and relates chiefly to the former of the two sources of glycogen just alluded to. The estimation of the glycogen was performed either by Brücke's or Külz's method. Large doses of different sugars were given. Dextrose, lævulose, cane sugar, and maltose increased the hepatic glycogen; lactose and galactose did not, or only very slightly.

The change which these sugars undergo in the alimentary canal was then investigated; cane sugar and maltose are inverted. Lævulose, lactose, and galactose are absorbed as such, and after

large doses pass as such into the urine. The liver appears unable to form glycogen from sugars which, like lactose and galactose, do not pass into the condition of either dextrose or lævulose. In fact, these appear to be the only forms of sugar which, when present in the blood, lead to the storage of glycogen in the liver. When subcutaneously injected, the hepatic glycogen rises in amount. No other form of sugar behaves in this way. Regarding lævulose, the liver cells must either form glycogen from it direct, or after previously changing it into dextrose. The latter possibility would not be improbable, as E. Fischer has shown; moreover, the action of the cells of the mammary gland in converting dextrose into lactose is somewhat analogous.

W. D. H.

The Behaviour of Milk Sugar in a Diabetic. By F. Voit (*Zeit. Biol.*, **28**, 353—360).—A diabetic patient was taking strict diet, and the amount of sugar in the urine reduced to a low ebb. On one occasion 100 grams, on another 150 grams, of milk sugar was administered; the sugar in the urine at once went up. A pure culture of *Saccharomyces apiculatus* was added to the urine, and fermentation allowed to go on. After a few days' fermentation, the urine contained no sugar. This fungus causes the alcoholic fermentation of glucose, but not of lactose. Thus there was no lactose in the urine. The dose given was not large enough to cause the appearance of this sugar in the urine. The explanation given of what had occurred is the following:—Before the sugar was given, the small amount of diabetic sugar in the urine must have originated from proteïd metabolism. Lactose appears in the urine more readily than any other form of sugar, not because it is burnt in the organism with greater difficulty, but as it is a form of sugar from which it is not possible for the liver to make glycogen, its "assimilation limit" is low, and so passes unused into the urine. In fact, in diabetics it appears to be more readily burnt in the body than dextrose, and takes the place of some of the dextrose originating from proteïd metabolism. Hence, when lactose is given, a large quantity of dextrose remains unburnt, and passes as such into the urine. W. D. H.

Transformation, in the Animal Economy, of Sulphanilic Acid into Sulphanilocarbamic Acid. By J. Ville (*Compt. rend.*, **114**, 228—231).—Sulphanilic acid was administered to dogs with their ordinary food; from the urine, part was recovered as an alkaline sulphanilate, and part as alkaline sulphanilocarbamate. This corresponds with the formation of taurocarbamic acid from taurine under similar circumstances (Salkowski, *Ber.*, **6**, 744).

For the extraction of the sulphanilocarbamic acid (Abstr., 1891, 1066), the urine is evaporated to a syrup, and treated with four or five times its volume of absolute alcohol. After standing for 24 hours, the precipitate is collected, washed with alcohol, and dried over sulphuric acid in a vacuum. It is then dissolved in a small quantity of water, and an excess of dilute sulphuric acid and alcohol is added. The precipitate is filtered off, and the filtrate evaporated over sulphuric acid to a syrup; this is diluted with water, neutralised with barium carbonate, filtered, and the barium precipitated by the calcu-

lated amount of sulphuric acid. Hydrochloric acid is removed by silver carbonate, and the liquid treated with hydrogen sulphide, filtered, and evaporated. The acid is dissolved out from the residue with absolute alcohol, the alcohol evaporated, and the residue decolorised by treatment with animal charcoal in aqueous solution, and finally evaporated over sulphuric acid in a vacuum.

Sulphanilocarbamic acid thus obtained crystallises in feathery plates, very soluble in water and absolute alcohol, completely insoluble in ether, chloroform, and benzene. The aqueous solution is decomposed by sodium hypobromite, with abundant evolution of nitrogen. When heated in a closed vessel at 135—140° with an excess of baryta-water, it decomposes with evolution of ammonia and formation of barium carbonate and sulphanilate.

Sulphanilic acid is obtained in brilliant, rhombic plates from the filtrate from the first alcoholic precipitation. W. T.

Decomposition of Fibrin, Gelatin, Peptone, and Asparagine in the Human Body. By L. Graffenberger (*Zeit. Biol.*, **28**, 318—344).—This investigation was undertaken in connection with Voit's theory of floating proteïd, to ascertain when the greatest rise of urea excretion occurred after the ingestion of nitrogenous material. The urine was collected at intervals of two hours; the diet was fixed, and on different occasions fibrin, gelatin, peptone, and asparagine were taken in addition. After taking fibrin, the increased output of nitrogen accounted for 49·2 per cent. of the fibrin taken. The greatest rise in urea occurred in the second period (that is, the third and fourth hours) after the meal. It fell somewhat in the third period, and after that fell rapidly. With gelatin, the same occurred, except that the fall after the fourth hour was more rapid. With peptone, the increase was as marked in the third as in the second period. With asparagine, there was a second rise, more marked than the first, in the fourth and fifth periods. W. D. H.

Influence of Water and Sodium Chloride on Nitrogenous Excretion. By D. Dubelir (*Zeit. Biol.*, **28**, 237—244).—Three experiments on a dog are recorded. The animal being in a state of nitrogenous equilibrium, it was found that water increased the volume of the urine, but did not alter the output of nitrogen. Sodium chloride also increased the volume of the urine, and lowered the excretion of nitrogen by 9 per cent. W. D. H.

Physiological Action of Gallic and Tannic Acids. By C. T. Mörner (*Zeit. physiol. Chem.*, **16**, 255—267).—Baumann and Wolkow (Abstr., 1891, 1129) have shown that homogentisic acid which occurs in the urine in cases of alcaptonuria, reduces an ammoniacal solution of silver nitrate, and this reaction serves for the estimation of the acid. The present investigation shows that it may also be applied to the estimation of gallic acid in the urine. By its means, a percentage of 0·001 of gallic acid, artificially mixed with the urine, can be recognised. The amount of ammonia used was 1 c.c. of the concentrated solution (or 3 c.c. of the 10 per cent. solution) to

10 c.c. of urine. The end reaction was ascertained by testing with hydrochloric acid the filtrate off from the reduced silver. From comparative experiments with normal urine, it is found necessary to deduct 1·3 c.c. of the silver solution used for 50 c.c. of urine.

When gallic acid is given by the mouth (to human beings and dogs) in small quantities, none appears in the urine; but, given in larger quantities, a certain amount passes as such into that secretion; thus, when 6, 4, 2, and 1 gram respectively are administered, 30, 20, 5, and 2 per cent. respectively appear in the urine. When tannin is given, none reappears as such in the urine; it seems to be entirely destroyed in the body; when large doses are given, however, a small quantity of gallic acid is found in the urine; when 8 to 10 grams are administered, only 1 per cent. is found as gallic acid in the urine.

Pyrogallol is not found. This coincides with some previous work of Stockman's (*Brit. Med. J.*, 1887, 1077). W. D. H.

Choline, Neurine, and Allied Compounds. By E. Schmidt (*Annalen*, **267**, 249—254).—On comparing the chemical constitutions of choline, muscarine, betaïne, and neurine, it is at once evident that apparently small differences in chemical composition and in structure have a very considerable effect on the physiological action of the compounds in question. In the case of neurine, $OH{\cdot}NMe_3{\cdot}CH{:}CH_2$, for example, it would seem that its poisonous action is closely connected with the presence of the vinyl group; consequently, it might be supposed that a compound of like nature, but containing an acetenyl in the place of the vinyl group, would be an equally powerful, or even a more powerful, poison. This view was put to the test of experiment, and found to be correct. *Acetenyltrimethylammonium hydroxide*, $OH{\cdot}NMe_3{\cdot}C{:}CH$ (compare Bode, this vol., p. 806), is a more virulent poison than neurine; on injecting only 1 milligram of this substance into the vein of a cat, respiration and the action of the heart immediately cease. *Allyltrimethylammonium hydroxide*, $OH{\cdot}NMe_3{\cdot}CH_2{\cdot}CH{:}CH_2$ (*loc. cit.*), on the other hand, is a relatively non-poisonous substance.

In order to ascertain the influence of the position, and of the number, of hydroxyl groups on the physiological action of compounds such as choline and muscarine, attempts were made to prepare isocholine, $OH{\cdot}NMe_3{\cdot}CHMe{\cdot}OH$, but without success; isomuscarine, $OH{\cdot}NMe_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, was, however, obtained without much difficulty (*loc. cit.*), and was found to have a strongly poisonous action, but quite a different one, in many respects, from that of muscarine.

F. S. K.

Chemistry of Vegetable Physiology and Agriculture.

New Method of Yeast Purification. By J. Effront (*Bull. Soc. Chim.* [3], **6**, 705—709; compare Abstr., 1891, 1532).—A complete temporary arrest of cell formation is caused by the addition of an alkali

fluoride (300 milligrams per 100 c.c. of wort), and yeasts so treated may be preserved for six months. On transference of the yeast to ordinary wort, the reproductive activity and the rate of alcohol formation increase; the results vary with the species of yeast employed, *S. cerevisiæ* affording the best results. Larger amounts of fluorides destroy the lactic and butyric bacilli, with but temporary effect on the yeast cells. Making use of the fact that the reproductive power of *S. cerevisiæ* is much more enhanced by fluorides than that of *S. Pastorianus*, the author finds that the treatment of three successive generations of mixed yeast cells, as above described, is sufficient to eliminate the latter variety. A comparative fermentation of a wort which with ordinary yeast lasted three days, but in the case of the same yeast, treated as above, was protracted during three weeks, resulted in favour of the prepared yeast, as judged by the density, limpidness, and taste of the beer. T. G. N.

Conditions influencing the Action of Fluorides on Fermentation. By J. Effront (*Bull. Soc. Chim.* [3], **6**, 786—793; compare preceding abstract).—The author details several experiments tending to prove that, in order to influence most favourably the suppression of the lactic and butyric fermentations, the wort to which the fluorides are added should be slightly acid, and that healthy development with increased reproductive activity of the yeast is assisted by the presence of alkaline phosphates, the maximum effect being attained at a temperature of 50—60°. T. G. N.

Nitrification in Organic Media of Acid Reaction. By E. Chuard (*Compt. rend.*, **114**, 181—184).—Turf-earth contains no nitrogen as nitric acid when freshly taken from its natural position. By exposure to the air, nitrification takes place to such an extent that a sample, containing no nitric acid to begin with, in the course of a twelvemonth was found to contain 0·298 per cent. N_2O_5.

The addition of chalk or potassium carbonate was found to exert a retarding effect on the nitrifying process; calcium sulphate exerted a similar action.

The nitrification, therefore, differs essentially from that taking place in arable soils, where a neutral or alkaline medium and comparative freedom from organic matter favour the process.

Whether the difference is due to the action of a different organism, or whether the process of nitrification is different from that obtaining in arable soils, has not yet been determined.

Encouraging results have been obtained by using turf-earth as a manure for vines, where it is essential to employ dressings rich in organic matter.

A cultivation of the organism in inorganic liquids has yielded a product in 10—15 days which gives the diphenylamine reaction; but no active nitrification, similar to that of the organism from arable soil, has been obtained. W. T.

Comparative Nitrification of Humus and Undecomposed Organic Matter. By P. Pichard (*Compt. rend.*, **114**, 490—493;

compare this vol., p. 656).—Humus is not readily attacked by nitrifying agents. The actual amount of nitrification is increased by the addition of calcium carbonate and sulphate, which hinder the volatilisation of the ammonia. The sulphate, however, can only be used for dry, porous soils, as in most soils the sulphide to which it is liable to be reduced is not reoxidised, and exercises, therefore, a retarding influence on the nitrification. In soils manured with undecomposed organic matter, such as seed-cake, the nitrification is much more rapid, and is still further facilitated by the addition of calcium sulphate. The proportion of nitrogen nitrified in vegetable soils containing 3—5 grams of organic nitrogen per kilogram is increased by diluting the soil with granitic sand, probably by facilitating aëration. In spite of the slow nitrification of humus, the amount of nitrates formed in sandy soils, poor in calcium salts, would be enough for the needs of the vegetation, were it not for the washing action of the rain. To increase the amount of nitrification, humus soils must, therefore, be mixed with calcium carbonate, a small amount of sulphate, and clay, or manured with compost mixed with calcium sulphate and loam. Jn. W.

Soluble Colouring Matters produced by Bacteria in Distilled Medicinal Waters. By L. Viron (*Compt. rend.*, **114**, 179—181).—Three pigments have been isolated from dark-green orange-flower water. One of these dissolves in water with a light-violet coloration, rapidly becoming brown in the air. It is without action on carbazole dissolved in concentrated sulphuric acid; by nitric and hydrochloric acids, its colour is changed to red. The second pigment dissolves in concentrated alcohol with a yellow colour; it is not influenced by nitric and hydrochloric acids, but, with carbazole in sulphuric acid, it gives a violet-blue coloration and then an indigo-blue precipitate. The third pigment is insoluble in methyl and ethyl alcohols, but dissolves in water with a fine, green coloration. It gives no reaction with the acids or carbazole. These colouring matters have been produced by the action of micro-organisms, which have been isolated by the author. The organism producing the first pigment is considered to be a variety of *Micrococcus cyaneus*. The organism yielding the yellow pigment has been named *Bacillus aurantii*. A third organism consists of small, spindle-shaped bodies, which tint gelatin green by reflected light but yellow by transmitted light; the pigment communicates an intense green coloration to water. An organism met with in much-altered waters produces a yellowish-green fluorescent coloration; it resembles *Bacillus fluorescens liquefaciens*.

W. T.

Vegetable Cell Membranes. By E. Schulze (*Zeit. physiol. Chem.*, **16**, 387—438).—The vegetable cell wall has a complicated composition. Some of the constituents, when heated with dilute mineral acids, easily yield galactose, mannose, arabinose, and xylose; others are not converted into glucoses unless concentrated mineral acids are employed, and the heating continued for some hours. The first group are named hemi-celluloses; the second, celluloses. One of the latter (dextroso-cellulose) yields dextrose, and is of wide distribution. In

some cases, celluloses yield mannose and xylose. The constituents of the cell wall are polymeric anhydrides of glucoses. It is impossible to say whether all these substances are merely mixed together or in a state of combination. Due regard must be paid to the probability that the reagents employed considerably alter the various materials present in the natural condition. W. D. H.

Occurrence of Mannitol and Sorbitol in the Fruit of the Cherry Laurel. By C. Vincent and Delachanal (*Compt. rend.*, **114**, 486—487).—Fully ripe cherry laurel fruit, gathered in September, was pounded into a paste, mixed with water, and allowed to ferment for some days. The mass thus obtained yielded a dark-red liquid, which, after clarification with lead acetate and removal of excess of lead, was concentrated in a vacuum to a syrup from which mannitol soon crystallised in characteristic long, silky needles.

The remaining syrup was treated with alcohol to precipitate the dissolved mannitol, the alcohol distilled off, and the residue treated with sulphuric acid and benzaldehyde. The resulting sorbitol benzoic acetal was then hydrolysed with dilute sulphuric acid, the acid removed by baryta, the sorbitol extracted with ether, and the ethereal solution evaporated in a vacuum to a syrup and allowed to crystallise. The sorbitol thus obtained was identical with that prepared from mountain ash berries. Jn. W.

Occurrence of Guanidine in Plants. By E. Schulze (*Ber.*, **25**, 658—661).—Vetch-seedlings, which had grown for three weeks in the dark, were dried, powdered, and digested with 92 per cent. alcohol. The filtered extract was distilled, the residue treated with water, and some tannin, and then lead acetate added. The precipitate was filtered off, and to the filtrate a solution of phosphotungstic acid added, and the precipitate collected, washed with dilute sulphuric acid, dried between filter paper, and decomposed with cold lime-water. The filtered solution was freed from lime by means of carbonic anhydride, again filtered, neutralised with nitric acid, and concentrated on the water-bath; crystals separated out which were shown to be identical in their properties with guanidine nitrate. 1 gram was obtained from 3 kilos. of dried seedlings. Lossen has shown that guanidine is formed in small quantity by the oxidation of proteïds, and it may perhaps have thus been formed in the seedling plant; it does not occur in vetch seeds which have not germinated.

C. F. B.

Vegetation of the Vine. By L. Roos and E. Thomas (*Compt. rend.*, **114**, 593).—During the first 10 or 12 weeks of vegetation, a saccharose exists in the leaves, sap, and even the grape, contrary to the opinion of Petit. This saccharose disappears during the fourth month of vegetation; the organs specified then contain a mixture of sugars, in which glucose predominates. The increase in the absolute amount of sugar does not correspond to diminution in acidity, and hence it is not always true that the acidity of fruits diminishes in proportion to the approach of ripeness. The diminution in the absolute acidity is observed at the moment when the amount of

levulose perceptibly increases in the fruit. At this point, the rotatory power changes in sign, and the lævorotatory power increases until the fruit is ripe, when it is practically identical with that of invert sugar. C. H. B.

Ammonia in Rain-water and in the Atmosphere. By A. Muntz (*Compt. rend.*, **114**, 184—186).—The author upholds the deductions drawn from determinations of the amount of ammonia in rain-water in tropical regions given in a previous paper (this vol., p. 381). He points out that the objections to these conclusions brought forward by Albert-Lévy (this vol., p. 381) are founded on observations taken in the neighbourhood of Paris, and quotes the results of Angus Smith, of Boussingault, and of the Rothamsted observations in support of the average value (0·50 milligram) of the ammonia per litre of rain-water adopted by the author for temperate climates. W. T.

Experiments on the Growth of Wheat in a Sterile Siliceous Sand. By A Pagnoul (*Ann. Agron.*, **17**, 538—544).—For the results of the 1890 experiments, see Abstr., 1891, 104. In 1891, similar experiments were instituted, cylinders of impermeable ware 13·6 inches high and of 120·64 sq. in. section being employed. The following results were obtained:—

1. Nitric nitrogen *versus* ammoniacal nitrogen.—When potassium chloride and soluble phosphate of lime were supplied as well, sodium nitrate was slightly better than its equivalent of ammonium sulphate, the respective yields of grain being in the ratio of 64·3 to 55·4.

2. Whereas the omission of potash reduced the yield in the ammonium sulphate pots in the proportion of 26 to 10, where sodium nitrate was employed, the reduction in yield by omitting potash was only in the proportion of 13 to 10. Potash increased the weight of the individual grain from 10 to 17 in the ammonium sulphate pots, from 10 to 14 in the sodium nitrate pots.

3. The addition of magnesium sulphate to the other chemical manures produced no effect.

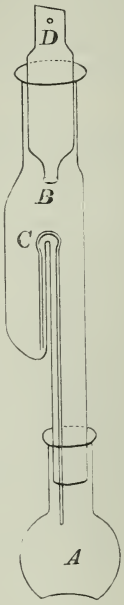
4. Arable soil—containing $CaCO_3$, 5·515; P_2O_5, 0·220; K_2O, 0·297; MgO, 0·297; and N, 0·139—was tried against the sterile sand. The soil pots were manured, once only, with sodium nitrate, containing 0·100 gram N, and superphosphate, containing 0·100 gram P_2O_5.

The sand pots were manured 20 times during the season, each receiving in the aggregate sodium nitrate containing 2 grams nitrogen and superphosphate containing 2 grams P_2O_5. Under these conditions the yield of grain in the soil was only 57 per cent., and of straw 68 per cent., of that in the manured sand. The grain grown in soil contained 12·93 per cent. proteïds, that in manured sand 15·77 per cent.

In the ammonium sulphate experiments the ratio of grain to straw was 55 to 100, and in the sodium nitrate experiments 64 to 100. These are both high yields, due to the abundance of soluble phosphate supplied in the manure. J. M. H. M.

Analytical Chemistry.

Extraction Apparatus. By J. T. Willard and G. H. Failyer (*Chem. Centr.*, 1892, i, 4; from *J. anal. Chem.*, **5**, No. 8).—The apparatus is easily understood from the figure. D is the lower end of the condenser, which is widened and ground to fit the upper part of the extractor; the lower end of the latter is ground to fit the flask.



The substance is placed in the side "pocket" C, and the siphon is loose. This must be bent as indicated, in order to prevent the extracting liquid from passing up the inner side by capillarity, and so over the bend and into the receiver before the "pocket" is full.

J. W. L.

Use of Bromic Acid in Quantitative Analysis. By W. Feit and K. Kubierschky (*Chem. Zeit.*, **15**, 351—352).—The authors have found that bromic acid, or, what amounts to the same thing, a solution of potassium bromate in dilute sulphuric acid, from which any free bromine may be expelled by boiling, is a very handy laboratory reagent. It acts as a powerful oxidiser, and the liberated bromine may be very readily expelled by boiling. The authors proceed in the following manner:—An accurately-measured excess of the bromate solution, which must contain excess of sulphuric acid, is put into a 200-c.c. flask, the substance is added, and the whole gradually

heated to boiling. After about five minutes, the bromine will be practically expelled, and no notice need be taken of a trace of a yellow colour. After cooling, the liquid is made up to the mark, and the excess of undecomposed bromic acid is estimated in an aliquot part of the liquid by means of potassium iodide and sodium thiosulphate. The authors communicate some very successful quantitative experiments. Hydrogen sulphide is oxidised to sulphuric acid and water. Sulphurous anhydride and hydrogen thiosulphate are also completely oxidised to sulphuric acid and water. Nitrous acid is oxidised to nitric acid, and oxalic acid is oxidised to carbonic anhydride and water.

The process may also be applied to ferrous salts. As the ferric compound obtained would interfere with the iodometric estimation, it must first be removed by a cautious addition of sodium carbonate. After making up to the mark and allowing to settle, the bromate may be estimated as usual after acidifying with sulphuric acid.

The authors have every reason to believe that bromic acid may become a useful reagent in the synthesis of organic compounds.

L. DE K.

Estimation of Fluorine. By A. CARNOT (*Compt. rend.*, **114**, 750—753).—The substance is heated with sulphuric acid and a large excess of silica in a carefully dried apparatus, and the silicon fluoride evolved is absorbed in a 10 per cent. solution of potassium fluoride, the end of the delivery tube being under mercury at the bottom of the vessel containing the fluoride solution. Potassium silicofluoride forms, and its precipitation is made more complete by adding an equal volume of alcohol of 90 per cent.; the precipitate is washed with alcohol and dried at 100° on a weighed filter.

The quantity of substance taken should not contain more than 0·100 gram of fluorine, and it must be intimately mixed with not less than 10 times as much finely-divided silica as there is fluorine present. About 40 c.c. of pure concentrated sulphuric acid is added, and the mixture is heated at about 160° in a carefully dried flask of 150 c.c. capacity, a slow current of dry carbonic anhydride being passed through the apparatus. The exit tube is furnished with a bulb to arrest any drops of sulphuric acid that may be spurted over, and if the substance contains chlorine, a tube containing anhydrous copper sulphate must be attached. Care must be taken that all the materials are free from fluorine, and, if necessary, a blank experiment may be made.

In order to estimate silica as well as fluorine, a known weight of pure silica is added to the substance, and the silica is determined partly by calculation from the weight of silicon fluoride and partly by direct separation from the residue in the flask, the weight of silica added being of course deducted. C. H. B.

Precipitation of Phosphorus from Solutions of Iron and Steel. By R. HAMILTON (*J. Soc. Chem. Ind.*, **10**, 904—906).—Shimer (Abstr., 1889, 76) suggested that the incomplete precipitation of phosphorus was due to incomplete oxidation, and proposed to render all the phosphorus precipitable by oxidising the solution with

potassium permanganate. The experiments recorded in this paper would appear to show that this view has much to commend it. They show (1) that the carbonaceous matter in a solution of iron does not prevent the complete precipitation of properly oxidised phosphorus as ammonium phosphomolybdate; (2) that the reason of the incomplete precipitation of phosphorus from a nitric acid solution of iron, which has not been evaporated to dryness and roasted, is that the phosphorus has not all been properly oxidised; and (3) that in such solutions all the phosphorus can be completely oxidised and rendered precipitable, in the wet way, by means of certain oxidising agents.

D. B.

Estimation of Phosphorus in Pig-iron by means of Braun's Centrifugal Apparatus. By C. Reinhardt (*Chem. Zeit.*, **15**, 410—412).—The author has found it quite possible to obtain, by this process, results which favourably compare with the gravimetric methods; but there is a great deal of personal equation in the matter, and every analyst should therefore fix his own coefficient, namely, the factor to be used in reducing the volume of the phosphomolybdate precipitate to percentage of phosphorus. L. de K.

Volumetric Estimation of Phosphoric Acid. By M. Spica (*Gazzetta*, **22**, i, 117—123).—The author employs the following process for estimating phosphoric acid in chemical manures. The weighed sample is cautiously heated with concentrated sulphuric acid in a small porcelain capsule until almost all the sulphuric acid is driven off; all the phosphoric acid is now in the free state, and is extracted from the residue by absolute alcohol, the metals remaining as sulphates insoluble in alcohol. The alcoholic solution is now filtered and evaporated on the water-bath to expel the alcohol. The residue is dissolved in water, rendered exactly neutral with soda, made up to a known volume, and an aliquot part taken for the titration. The solution is titrated in the cold with standard potassium ferric alum solution. On running in the ferric solution, a white precipitate of ferric phosphate separates. Aqueous salicylic acid solution is used as the indicator; an amethyst colour is produced when excess of iron is added. The solution must be exactly neutral when titrated, for if it be alkaline, ferric hydroxide will be precipitated, whilst, if acid, part of the ferric phosphate will be dissolved. 1 c.c. of the ferric solution may conveniently be made equivalent to 1 milligram of P_2O_5. The results are very good. W. J. P.

Analysis of Phosphates. By J. H. Vogel (*Chem. Zeit.*, **15**, 495—499).—The author, who has made a thorough investigation of the matter, comes to the conclusion that, in order to get a trustworthy estimation of iron and alumina in phosphates, Glaser's process should be used in conjunction with Stutzer's method. The first process generally gives the results too high, on account of co-precipitated magnesia; the second process gives the results too low, on account of the slight solubility of the phosphates in acetic acid.

The author first throws down the aluminium and ferric phosphates according to Glaser's directions, but does not boil the ammo-

niacal fluid to redissolve the magnesium phosphate. The precipitate is now treated according to Stutzer's plan, namely, separation of the phosphoric acid with molybdate and precipitation of the joint ferric and aluminium hydroxides with ammonia. The magnesia remains in solution. A second precipitation frees the precipitate from any molybdate. In this way, absolutely correct results may be obtained.

L. DE K.

Estimation of Carbon in Iron and Steel. By W. THÖRNER (*Chem. Zeit.*, **15**, 149).—The author strongly objects to Rürup's proposal of using india-rubber connections when oxidising the well-known copper carbon mixture with sulphuric acid and potassium dichromate. If the operator wishes to use a flask which may be readily disconnected from the condenser, an ingenious contrivance devised by the author may be employed. L. DE K.

Detection and Estimation of Potassium Spectroscopically. By F. A. GOOCH and T. S. HART (*Amer. J. Sci.*, **42**, 448—459).—The authors have endeavoured to improve the delicacy of the spectroscopic potash test by making use of more powerful flames, and by substituting hollow coils of platinum wires for the single loop. Such coils are easily made by winding the wire somewhat obliquely around a rod of suitable size, pressing the coils close together, and joining the free ends into a twisted handle. The size of the coils is adjustable without difficulty, so that each coil may be made to hold almost exactly any appropriate amount and to take up this amount with very little variation in successive fillings, provided only that the precaution be taken in the process of filling to plunge the coil while hot into the liquid and to keep its axis inclined obliquely to the surface of the liquid while withdrawing it. In these coils we have simple means of taking up known amounts of solution, and this may be evaporated with little danger of loss of solid material by holding the handle of the coil across the flame with the coil proper at a safe distance outside. The burner used in heating the coils is of the Muencke pattern, and gives a powerful flame 3 cm. wide at its base. The authors generally adjust the flame to a height of 20 cm., and introduce the dried coil just within the outer mantle on the side next the spectroscope, with the axis transverse to the slit of the spectroscope and the handle across the body of the flame.

The spectroscope recommended is a well-made single-prism instrument provided with a scale and a movable observing telescope, so that different portions of the spectrum may be viewed or cut off at will. The slit is adjustable, but, for measuring its width, the authors have been obliged to have recourse to the device of closing it upon wires of known gauge. If a quantitative estimation is intended, a standard solution of potassium chloride, containing 0·002 milligram of potassium to the coilful, is tested in the apparatus, and the liquid under examination is diluted until its potassium line is of the same brightness as that given by the same quantity of the standard solution. The calculation presents, of course, no difficulty. If the substance contains sodium, this causes a remarkable increase in the

brightness of the potassium line, the maximum effect being reached when it exceeds the potassium by 100 to 1. In this case, a judicious quantity of sodium chloride should be added to the standard solution. Too large a proportion of sodium chloride in the sample is, however, undesirable, and may be got rid of by precipitation with alcohol.

To ensure success, it is essential that the eye of the observer should be kept as near as possible in the same condition of sensitiveness and in the same position in making the comparisons, and to accomplish this it is best to hold the eye at the observing telescope during the entire interval between the exposures, to shade it carefully by the hand or otherwise, to cover the eye not in use, to cut off all direct sunlight from the work-table, and to light the comparison scale of the spectroscope to the faintest possible visibility in order to fix exactly the position in which the line is to be sought.

The test analyses are encouraging. Though not accurate to a very high degree when large amounts of potassium are to be estimated, the method offers great advantage, without much sacrifice of exactness, in the estimation of small quantities. L. DE K.

Estimation of Small Quantities of Calcium. By M. KRÜGER (*Zeit. physiol. Chem.*, **16**, 445—452).—It is shown that Hempel's method of estimating calcium by titration of its oxalate with potassium permanganate solution is one which is applicable to such small quantities of calcium as often have to be dealt with in the operations of physiological chemistry. W. D. H.

Solubility of Calcium and Strontium Chromates in Dilute Alcohol, and the Separation of these two Alkaline Earths as Chromates. By W. FRESENIUS and F. RUPPERT (*Zeit. anal. Chem.*, **30**, 672—680).—An aqueous solution of the chlorides (containing preferably not more than 3 per cent.), mixed with potassium chromate, warmed to 60—70°, and mixed with one-third of its volume of strong alcohol, gives a precipitate almost instantly when strontium is present, but none in its absence, or only after a long time a trifling one, which cannot be mistaken for the strontium precipitate. About 0·0004 gram of strontium chloride per c.c. appears to be the lower limit of detection, in the presence of six times as much calcium chloride (see Lüdeking, Abstr., 1891, 364). A larger proportion of alcohol should be avoided; with 6 vols. of alcohol to 10 of the aqueous solution, calcium chromate began to precipitate. The method can be used only for rough quantitative separation; 50 c.c. of alcohol of 29 vols. per cent. dissolve 0·0066 gram of strontium chromate, or 0·608 gram of calcium chromate. In alcohol of 53 vols. per cent., the solubility is 0·44 gram of calcium chromate and 0·001 of strontium chromate in 50 c.c.

For qualitative analysis, the two bases should be precipitated as carbonates, the precipitate dissolved in hydrochloric acid, the excess of acid evaporated off, and the dilute aqueous solution mixed with potassium chromate and one-third its volume of alcohol, and shaken. M. J. S.

Separation of Strontium and Calcium Nitrates by means of Amyl Alcohol. By P. E. Browning (*Amer. J. Sci.*, **43**, 50—56).—The author, having found that calcium nitrate is completely soluble in amyl alcohol, whilst strontium nitrate is practically insoluble, has based on this fact a quantitative separation of the two metals. To ensure success, the operation must be conducted as follows:—About 0·5 gram of the mixed nitrates is dissolved in the smallest possible quantity of water and boiled with 30 c.c. of amyl alcohol until this reaches its normal boiling point, showing that all moisture has evaporated. The solution is then filtered from the undissolved strontium nitrate through asbestos, and this is washed with anhydrous amyl alcohol contained in a wash-bottle, the mouth-piece of which consists of a small calcium-chloride tube passing through the stopper and drawn out and plugged at the lower end with cotton-wool. To make sure of a complete separation, it is advisable to dissolve the residue in water and a drop of nitric acid, to evaporate to dryness, and to treat the nitrate again with amyl alcohol, in the manner described.

The strontium is finally converted into sulphate, and weighed as such. The united alcoholic filtrates containing the calcium are evaporated to dryness, and the residue is then also converted into sulphate.

In accurate analysis, it must be remembered that strontium nitrate is not absolutely insoluble in amyl alcohol. The author therefore proposes to add 0·001 gram of strontium oxide for every 30 c.c. of amyl alcohol employed. A corresponding amount of strontium sulphate must, of course, be deducted from the weight of the calcium sulphate. L. de K.

Separation of Barium from Calcium. By P. E. Browning (*Amer. J. Sci.*, **43**, 314—317).—The fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol (compare preceding abstract) naturally suggested a similar separation of barium from calcium by the same general treatment. The author found that barium nitrate is totally insoluble in amyl alcohol, so no correction for slight solubility is required, as in the case of strontium. In the separation of the latter substance from calcium, it is necessary to have recourse to a double treatment with amyl alcohol, in order to effect a complete separation, because the strontium nitrate separates in plate-like masses, whilst the barium salt is much more granular and less liable to include foreign matter, and is, therefore, obtained pure by a single treatment.

The rapidity of execution and satisfactory character of the test analyses seem to place the process among the good analytical methods for the separation of barium and strontium from calcium.

L. de K.

Estimation of Zinc by the Ferrocyanide Process. By F. Moldenhauer (*Chem. Zeit.*, **15**, 223—224).—The estimation of zinc by means of potassium ferrocyanide, with copper sulphate paper as indicator, is gradually superseding the old process with sodium sulphide, but certain precautions should be taken to avoid errors.

The standard solution of ferrocyanide is best made of such a strength that 1 c.c. equals 0·005 gram of zinc. This solution does not keep well, but decomposition may be retarded by the addition of 1 gram of potassium hydroxide per litre, and keeping the liquid in the dark. The author has investigated the influence of the presence of some other metals which are often associated with zinc. Of the alkaline earths and the lighter metals, there exist only two whose ferrocyanides are quite insoluble in ammonia, namely, zinc and manganese, whilst magnesia is sparingly soluble. In the presence of these two metals, the amount of zinc may be found from 3 to 6 per cent. too high. The author has therefore modified the process as follows:—2·5 grams of the zinc ore is dissolved in hydrochloric acid, oxidised with nitric acid, and, without filtering, diluted to 250 c.c. 50 c.c. of this solution is heated and mixed with 10 c.c. of ammonia and 5 c.c. of a solution containing, in 100 c.c., 5 grams of ammonium chloride, 5 grams of ammonium carbonate, and 10 c.c. of ammonia. While the mixture is cooling, 50 c.c. of the original liquid is mixed with 10 c.c. of ammonia and carefully titrated with the ferrocyanide.

When cold, 1 c.c. of a 10 per cent. solution of disodium hydrogen phosphate is added, which will precipitate any manganese or magnesia as phosphate. The titration is now most carefully repeated, and will, of course, often give a lower result than the first.

The test analysis, made on an artificial zinc ore, is very satisfactory.

L. de K.

Estimation of Manganese in Iron and Steel. By L. Rürup (*Chem. Zeit.*, **15**, 149—150).—The author has modified the process as follows:—6 grams of the sample is dissolved in acid as usual, and, after oxidation, introduced into a litre flask. After the addition of some sodium sulphate, water is added up to the mark, and, after settling, the liquid is filtered through a double quick filter. 500 c.c. of the filtrate (= 3 grams of substance) is put into a 1-litre Erlenmeyer flask, mixed with zinc oxide, heated, and titrated with permanganate.

The advantage of the process is supposed to consist in the large quantity of material operated on. L. de K.

Separation of Iron, Manganese, and Calcium by the Acetate and Bromine Methods. By R. B. Riggs (*Amer. J. Sci.*, **43**, 135—140).—The author, after conducting a great number of experiments, concludes that, in precipitating iron as a basic acetate, it is probably better to avoid a large excess of alkaline acetate, and the precipitate should not be digested too vigorously or too long. When the solution is neutralised previous to the acetate separation, there is always a danger of some of the manganese separating out as a higher oxide, but the amount is generally trifling, and may be completely recovered by redissolving and reprecipitating the iron.

In the subsequent separation of the manganese from the calcium, the filtrate from the iron should be mixed with excess of ammonia and heated, before adding the bromine, as, if the solution is cold, the oxidation is slow and incomplete. The addition of ammonia after the bromine has been added causes a less uniform oxidation. To free the manganese from co-precipitated calcium, it must be re-

dissolved in hydrochloric acid, and again precipitated with ammonia and bromine. The calcium is finally precipitated as oxalate.

L. DE K.

Electrolytic Separation of Iron. By E. F. SMITH and F. MUHR (*Chem. Centr.*, 1892, i, 75; from *J. Anal. Chem.*, **5**, 488).—If a solution of ammonio-ferrous tartrate be subjected to the action of a feeble voltaic current (equivalent to the liberation of about 3 c.c. of oxyhydrogen gas per minute), the iron separates in a very compact form, but contains some carbon. In one experiment, 0·161 gram of iron as ferrous sulphate, with 1 gram of tartaric acid and 10 c.c. of ammonia in 150 c.c., was subjected to such a current for 20 hours, when the precipitated iron weighed 0·165 gram. After dissolving in sulphuric acid, titration with potassium permanganate showed 0·161 gram of iron to be present. The method may be employed for the separation of iron from aluminium. Nickel, cobalt, zinc, copper, and cadmium are precipitated quantitatively under the above conditions.

J. W. L.

Estimation of Cobalt in Manganese Ores. By T. MOORE (*Chem. News*, **65**, 75—77).—Two grams of ore is fused in a covered platinum crucible with 4 or 5 grams of potassium hydrogen sulphate; when the fusion becomes quiet, in 15—20 minutes, ammonium carbonate is added in successive small quantities, replacing the cover after each addition until sulphuric anhydride is emitted but feebly; the mass is then poured on to a metal slab, and when cool is put along with the rinsings from the crucible into 400 c.c. of boiling water. After boiling for 20 minutes, and boiling and washing the insoluble residue several times with hot water, the combined filtrates are heated, 30 c.c. of acetic acid added, hydrogen sulphide passed in, and, when the iron still remaining in solution is reduced, a strong solution of ammonium acetate is added. The precipitated sulphides of nickel and cobalt, after being well washed, are calcined at a temperature just sufficient to destroy the filter, and are dissolved in a few c.c. of hydrochloric acid, and converted into sulphates by evaporation with sulphuric acid. The two metals are then deposited together electrolytically in the usual manner, and, their weight having been determined, they are redissolved and separated, preferably by precipitating the cobalt as phosphate.

A second method, based on the fact that cobalt alone absorbs oxygen to any appreciable extent in the presence of citric acid, is conducted by evaporating 2 grams of ore to dryness with hydrochloric acid, then mixing with 3 grams of citric acid dissolved in 3 or 4 c.c. of ammonia, and, if necessary, acidifying with hydrochloric acid; after heating with 2 or 3 c.c. of water and allowing it to cool, the solution is transferred to and agitated in a modified Bunte's gas burette, the amount of oxygen absorbed being subsequently noted with every precaution.

D. A. L.

Estimation of Molybdenum. By E. PÉCHARD (*Compt. rend.*, **114**, 173—175).—Hydrogen chloride is passed over the molybdate at 440°. The base remains in the boat as chloride, and the molybdenum collects in the tube in white needles, having the composition

$MoO_3,2HCl$; this is dissolved in water, and the solution evaporated to dryness, when the residue consists of molybdic anhydride. A small quantity of a bluish sublimate, insoluble in water, is easily dissolved by adding a little nitric acid to the wash water, and is then weighed, with the main residue, as trioxide. The trioxide is obtained directly from ammonium molybdates by simply heating at 440°. As tungstates do not give a volatile compound similar to the above, the determination of molybdenum, in presence of tungsten, can be carried out by this method. The results of trial analyses quoted show the method to be trustworthy. The volatile compound is formed, even in the cold, by passing hydrogen chloride over a molybdate. The ethereal extract of the residue deposits white crystals, consisting of the volatile compound and ether. W. T.

Detection of Tin, Antimony, and Arsenic. By E. Pieszczek (*Arch. Pharm.*, **229**, 667—669).—After separating the sulphides of arsenic, antimony, and tin from the other sulphides of the hydrogen sulphide group by means of ammonium or potassium sulphide solution, the author precipitates the mixed sulphides with hydrochloric acid, and then separates the arsenic sulphide with ammonium carbonate. The antimony and tin sulphides are then dissolved in concentrated hydrochloric acid (without addition of potassium chlorate), and to a drop of the solution placed on a platinum crucible lid, a small piece of tin is added; any antimony is precipitated on the platinum as a brown or black deposit. If a trace of copper should be present, it is likewise precipitated, but the deposit is red, and has a metallic lustre, which is readily distinguishable from the antimony.

For the detection of tin, a piece of iron wire is placed in another portion of the solution of antimony and tin; any antimony which is present is precipitated, whilst the tin is reduced to stannous chloride, and may be detected by means of mercuric chloride. J. W. L.

Assay of Antimony Minerals. By A. Carnot (*Compt. rend.*, **114**, 587—590).—The antimony is dissolved in hydrochloric acid, precipitated by tin, and weighed in the metallic state. In the case of sulphuretted minerals, a quantity containing about 1 gram of antimony is heated with successive quantities of strong hydrochloric acid until the whole of the sulphide is decomposed. The last quantity of acid is mixed with a small quantity of nitric acid, and the residue is washed with dilute acid. The extraction is effected on a water-bath, but actual ebullition should be avoided. The decanted or filtered solution is diluted with an equal volume of water, a piece of sheet tin is added, and the liquid is heated at about 80° or 90°. The precipitated antimony is washed with dilute hydrochloric acid, then with warm water, and, finally, alcohol, and is weighed on a tared filter.

Oxidised minerals are placed in a flask with a flat bottom, heated at a temperature not exceeding 300°, and subjected for about an hour to the action of a current of hydrogen sulphide. The antimony is thus converted into sulphide, which is then dissolved (in the same flask) in the manner just described.

Iron and zinc do not interfere with the estimation. Lead is

partially precipitated with the antimony, but, after weighing, it may be separated and estimated by treating the metals at 50—60° with a yellow solution of sodium polysulphide (obtained by boiling a solution of the monosulphide with sulphur), which dissolves the antimony, and leaves a residue of lead sulphide. The latter is washed, dried, and weighed: 0·9 of the weight of the precipitate gives the quantity of metallic lead present in the mixture of metals.

C. H. B.

Estimation of Bismuth in Silver Slags. By W. Hampe (*Chem. Zeit.*, **15**, 410).—1 gram of the finely powdered slag is digested in a platinum dish, first with 15 c.c. of nitric acid, then with 10 c.c. of strong hydrofluoric acid; if everything is dissolved, a few drops of sulphuric acid is added, and the whole evaporated to dryness. The residue is again dissolved in nitric acid, filtered from any graphite, and after neutralising the filtrate with ammonia, ammonium carbonate is added, and the liquid heated to boiling. The precipitate is then collected, redissolved in dilute nitric acid, and treated with hydrogen sulphide. The precipitate, which consists of lead and bismuth sulphides, is again dissolved in nitric acid, filtered from any sulphur, once more precipitated with ammonium carbonate, the precipitate dissolved in hydrochloric acid, and the liquid evaporated to dryness. On treating the residue with boiling water, the lead chloride is gradually dissolved, whilst the bismuth remains as oxychloride; this is then dissolved in nitric acid, and precipitated with ammonium carbonate. The precipitate is afterwards carefully detached from the filter and temporarily put aside; the filter is extracted with nitric acid, and this is evaporated to dryness in a weighed porcelain crucible. The precipitate is now added, the whole carefully ignited, and finally weighed as bismuth oxide.

L. de K.

Use of Cadmium in Assaying Gold. By C. Whitehead (*Proc. Chem. Sect., Franklin Inst.*, **3**, 94—98).—An approximate assay of the silver in the gold bullion is first made by cupellation. 500 milligrams of the bullion is then placed in a porcelain crucible, covered with 10 grams of potassium cyanide, and heated until the cyanide is in a state of quiet fusion. 1 gram of cadmium is then added; it forms a bright, homogeneous alloy with the gold; if no copper is present in the bullion, about 50 milligrams is added, in order to make the resulting alloy brittle. The contents of the crucible are poured on to a porcelain slab, the alloy is washed, dried, placed in a diamond mortar, and reduced to a powder by a few sharp blows with a hammer. The powder is then transferred to an assay bottle, sufficient pure silver is added to make the total amount present 1004 milligrams (the amount in the bullion itself has been approximately determined by the preliminary cupellation), and 10 c.c. of nitric acid (32° Baumé) added. To this solution 100 c.c. of normal salt solution is added, and the precipitation is finished with a decinormal salt solution. The assay is accompanied by another "proof" assay, in which 1004 milligrams are dissolved in the same amount of acid. The difference in the amounts of salt solution used gives the excess of silver in the assay over that in the "proof." Adding this to 1004 milligrams, the

amount in the "proof," we get the total amount in the assay; subtracting from this the weight of pure silver added in the assay, we get the weight of silver in the 500 grams of bullion used. An actual assay gave 38 parts per thousand, as against 35 determined by cupellation. C. F. B.

Electrolytic Separations. By E. F. Smith and D. L. Wallace (*Ber.*, **25**, 779—785; compare Abstr., 1891, 1029).—The metal which is mentioned first in each of the following cases, is deposited on electrolysis:—

Gold from Arsenic.—The metallic salts were dissolved in potassium cyanide solution; the deposited gold is pale yellow. The results are satisfactory with currents evolving 1·8—2 c.c. of oxyhydrogen gas per minute.

Gold from Molybdenum.—Results excellent. The gold is deep orange-yellow in colour.

Gold from Tungsten.—Results fairly good, if the solution is free from potash; otherwise, as separate experiments have shown, the precipitation of the gold is very incomplete.

The separation of the above metals in potassium cyanide solution compares unfavourably with their separation from solution in alkaline sulphides, chiefly on account of the length of time required, 10—16 hours.

Gold from Osmium.—Results very satisfactory. A current evolving 2·4 c.c. oxyhydrogen gas per minute is required.

Cadmium from Osmium.—Results good; excess of potassium cyanide is to be avoided.

Silver from Osmium.—Results extremely satisfactory; time required about 7 hours.

Mercury from Osmium.—Results excellent; a current evolving 0·7—1·9 c.c. of mixed gases per minute is needed.

Cadmium from Nickel.—Results very good; the mixed solutions of cadmium and nickel sulphates are treated with potash, and a current evolving 2 c.c. of oxyhydrogen gas per minute is employed.

The fact noted above, that potash hinders the precipitation of gold, caused the authors to attempt to separate silver and mercury from gold, but the experiments were unsuccessful.

It was also found impossible to cause the complete deposition of gold from solution in ammonium sulphide, whilst attempts to separate gold from tin in ammonium sulphide solution were also fruitless.

J. B. T.

Assaying of Platinum. By F. Mylius and F. Foerster (*Ber.*, **25**, 665—686; see this vol., p. 789).

Estimation of the Dissolved Substances in Water. By A. Hazen (*Chem. Centr.*, 1892, i, 74; from *J. Anal. Chem.*, **5**, 140).—The author recommends the addition of sodium carbonate to the water before evaporating, in order to avoid the presence of water of combination in the magnesium and calcium chlorides, or the loss of hydrogen chloride, when heating the residue over the flame.

J. W. L.

Volatile Organic Matter in Potable Water and a Simple Method of Estimating Dissolved Fixed and Volatile Organic Matter in Water. By W. C. Young (*J. Soc. Chem. Ind.*, **10**, 883—889).—To determine the total organic matter, 1 litre of water, to which 0·5 gram of dried and ignited sodium carbonate is added, is distilled in a conical iron still of about 2 litres capacity, attached to a tin worm-condenser. The distillate is received in a graduated measure, and when 970 c.c. has been collected, the source of heat is removed, the still disconnected, the contents and washings placed in a platinum basin, and evaporated to dryness on a water-bath. The residue is then dissolved in a little pure distilled water, filtered through an asbestos plug into a platinum basin, dried on a water-bath, and subsequently heated for an hour in an air-bath at 150°. After cooling in a desiccator, the basin and contents are weighed. The residue is then ignited at a low temperature, cooled, and weighed, and the loss noted. The ignited residue is dissolved in water, excess of sulphuric acid added, and then standard solution of potassium permanganate (1 c.c. = 0·0001 gram O) until the colour remains permanent after five minutes. The weight of oxygen lost, thus ascertained, is deducted from the loss on ignition, and the difference is the organic matter. To determine the fixed organic matter, the same course is followed, except that the sodium carbonate is not added until the concentrated water is transferred from the iron still to a platinum basin. To determine the volatile organic matter, the distillate from the last-mentioned process is placed in the still, together with 0·5 gram of sodium carbonate, and distilled until about 25 c.c. remains in the still, afterwards proceeding as before, except that it is unnecessary to ascertain the oxygen lost by ignition. The result presents about two-thirds of the total volatile organic matter present; further small quantities can be recovered from the distillate by repeating the process.

By the employment of sodium carbonate the whole of the compounds of calcium, magnesium, and iron are precipitated, and any combined ammonia in the water is volatilised. There only remains sodium chloride, alkali nitrates, and uncombined silica to interfere with the loss on ignition being accepted as a measure of the organic matter present, and neither of these compounds being present in estimating volatile organic matter, the results may be accepted as free from objection on that account. As regards sodium chloride, the burning of the organic matter is so rapid (a few seconds suffices), and the temperature so low, that none is volatilised, or if a little is lost through excessive heating, the loss can be ascertained and due correction made. As regards alkali nitrates, provision is made in the process for ascertaining and correcting for loss of oxygen by reduction of nitrates, but it is seldom of any great importance, and has never exceeded, in ordinary drinking waters, the equivalent of 0·07 grain per gallon. The presence of nitrates assists the burning of the organic matter very materially, and in the case of very foul waters, such as sewage effluents or seriously polluted waters, which rarely contain any, the author finds it advisable to add a drop or two of solution of potassium nitrate before the final evaporation. With

regard to the uncombined silica, the author has never found it present, and if it should be, he does not think the heat required to burn off the organic matter is sufficiently great to cause it to decompose the sodium carbonate. D. B.

The Fermentability of Dextrins. By L. Medicus and C. Immerheiser (*Zeit. anal. Chem.*, **30**, 665—668).—Some specimens of wine, which the authors had condemned as adulterated with potato-starch sugar, were by other analysts described as genuine on the ground of the complete fermentability of their dextrorotatory constituents. The authors confirm the fact of this complete fermentation under the influence of pressed yeast. It takes place, however, very slowly. Specimens exhibiting originally a dextrorotation of 0·45—0·83° lost this entirely in from 25—28 days after mixing with pressed yeast. That the substances so fermented were dextrins was shown by the behaviour towards Fehling's solution after inversion, a much greater increase in the reducing power being found after treatment capable of saccharifying dextrin than after simple inversion of the cane sugar present. These results were confirmed by experiments on commercial potato-starch sugar. 250 c.c. of a 16 per cent. solution mixed with a little ammonium and potassium phosphates, and 2 grams of pressed yeast, fell off in rotating power from 17° to 7° in 11 days at ordinary temperatures, and on further addition of yeast and elevation of the temperature to 30°, the polarisation was finally reduced to about 1° in the course of 34 days. In a second experiment on solutions of the same strength without phosphates, but with more yeast, the rotation fell to 0 after the lapse of 32 days. In a third experiment, dextrin precipitated by alcohol from potato-starch sugar, and thoroughly washed with alcohol, was employed with a precisely similar result. The conclusion arrived at is that dextrin, although with difficulty, is yet completely fermentable under the influence of vigorous pressed yeast and at a favourable temperature.

M. J. S.

Recognition of Potato-starch Sugar in Wines. By W. Fresenius (*Zeit. anal. Chem.*, **30**, 669—672).—The statement of Neubauer that the substances precipitable from potato-starch sugar were not fermentable having been based on experiments with beer yeast, and the investigations of v. Raumer having shown that the behaviour of these substances was not identical with different kinds of yeast, the following further experiments were made:—A specimen of one of the dextrorotating wines examined by Medicus (see preceding abstract), and an optically inactive wine, were evaporated to syrups, and mixed, the former with a 10 per cent. solution of completely fermentable invert sugar, and the latter with a 10 per cent. solution of potato-starch sugar containing so-called "unfermentable substances." Under the influence of pressed yeast at 30°, both lost their rotating power completely in four days. In a similarly conducted experiment with a non-polarising wine mixed with potato-starch sugar and beer yeast, the solution still showed a rotation of 5° after 13 days. Specimens of the suspected wines were therefore evaporated, and mixed with fermentable invert sugar and beer yeast. The

observed result is not given, but it is stated that a thoroughly satisfactory proof was obtained that potato-starch sugar had been introduced into the wines. In the course of the experiments, it was observed that the wines were very apt to become mouldy on the surface, and after the growth of mould the dextrorotatory constituents were found to have disappeared. The same was the case with nitrates, which had been detected by Medicus and Immerheiser, but had disappeared by the time the samples were examined by the author (see also Borgemann, Abstr., 1888, 753). M. J. S.

Estimation of Cellulose. By S. Gabriel (*Zeit. physiol. Chem.*, **16**, 370—386).—Hönig's method of estimating cellulose (*Chem. Zeit.*, 1890, 53) by dissolving out proteïd and starch with glycerol at 210° gives results which are too high, the residue being rich in ash and containing about 1 per cent. of nitrogen, as well as certain non-nitrogenous substances which are not cellulose. A number of comparative experiments were made with different agricultural products, and the commonly used Weender method was found to give more trustworthy results. A solution of potassium hydroxide in glycerol, heated to 150°, was, however, found to give approximately correct results.

W. D. H.

Detection of Resin Oil in Terebenthene. By Zune (*Compt. rend.*, **114**, 490).—The terebenthene is fractionated, and the refractive index of the various fractions determined. In the absence of resin oil, the difference between the indices of the extreme fractions should not exceed 0·004, whilst in the presence of even 1 per cent. of the oil it is at least 0·006. Jn. W.

Detection of Resin in Beeswax. By H. Röttger (*Chem. Zeit.*, **15**, 45).—If a sample of wax contains not less than 5 per cent. of resin, it will, on heating it to 110°, emit a strong odour of turpentine, but pure wax collected in the neighbourhood of pine woods also gives this test. If the amount of resin is large, any expert will notice this from the very appearance of the sample, but small quantities are best detected by a process recommended by Donath. A piece of the suspected sample the size of a pea is put into a test-tube and boiled for 15 minutes with strong nitric acid. A little cold water is carefully added to solidify the wax, and the acid liquid poured into excess of dilute ammonia, which, if resin is present, will cause a blood-red coloration. Schmidt recommends boiling 5 grams of the wax for one minute with 25 grams of nitric acid (sp. gr. 1·33). He then adds an equal bulk of cold water, and afterwards a slight excess of ammonia. If the sample contains resin, the colour of the liquid will be reddish-brown. Hager boils the sample with 15 times its weight of dilute alcohol (2 vols. of alcohol, 1 vol. of water). After cooling, the liquid is filtered and diluted with an equal bulk of water, which, if resin be present, will cause a white emulsion. Stearic acid does not interfere with the test. The German Pharmaceutical Committee recommends boiling the sample for 15 minutes with 10 parts of water and 3 parts of sodium carbonate, when, if resin be present, a permanent emulsion will be obtained. Sedra dissolves 3 grams of the sample in 30 c.c. of

chloroform, and then shakes this with 200 c.c. of lime-water; pure wax forms an emulsion, but, if resin is present, a turbid, yellowish-brown liquid separates out.

The author, who carefully tried these processes, failed to detect an admixture of 20 per cent. of resin by Sedra's process. Hager's method gives satisfactory results if a weaker alcohol (1 vol. alcohol, 1 vol. water) is used. Donath's process is best applied to the spirituous extract of the sample. L. de K.

Sodium Nitroprusside as a Reagent for Aldehydes and Ketones. By B. v. Bittó (*Annalen*, **267**, 372—379).—The author has investigated the behaviour of a large number of aldehydes and ketones towards sodium nitroprusside in alkaline solution, and gives his results in a table. It was found that a coloration is produced in the case of all aldehydes and ketones of the fatty series when the aldehyde or carbonyl group is in direct combination with at least one group composed only of carbon and hydrogen; acetaldehyde, acraldehyde, and chloracetone, for example, give a cherry-red, and paraldehyde a reddish-yellow, coloration, but formaldehyde, glyoxal, and chloral give no reaction. Aromatic aldehydes or ketones, in which the aromatic radicle is combined only with the aldehyde or carbonyl group, as, for example, in the case of benzaldehyde and benzophenone, do not give the reaction; when, however, the aromatic radicle is also united with a fatty hydrocarbon radicle, as in paracumaldehyde, a coloration is produced. More definite statements regarding the behaviour of the aromatic compounds cannot be made for want of experimental data. F. S. K.

Estimation of Cinnamaldehyde in Oil of Cassia. By Schimmel (*Chem. Centr.*, 1892, i, 92—93; from *Schweiz. Wochenschr. Pharm.*, **29**, 403).—The authors recommend the following method as being more rapid than that usually employed:—10 c.c. of the oil is heated in a small flask on the water-bath, and solution of sodium hydrogen sulphite is added in small portions, time being allowed between each addition for the mass, which at first forms, to liquefy again. The time required amounts to 10—15 minutes. (Compare Abstr., 1891, 504.) J. W. L.

Estimation of Free Acids in Butter. By C. Besana (*Chem. Zeit.*, **15**, 410).—The author extracts the butter with alcohol, which, at a gentle heat, easily dissolves the free acids, but scarcely touches the glycerides. 10 grams of the clarified fat is treated three times in succession with 15 c.c. of rectified spirit at a temperature of about 50°. The mixed alcoholic liquids are afterwards titrated with N/10 sodium hydroxide, with phenolphthaleïn as indicator.

From the author's experiments, it is made plain that rancid, unsaleable butter does not necessarily contain the largest proportion of free acids. L. de K.

Estimation of Gallic Acid in Urine. By C. T. Mörner (*Zeit. physiol. Chem.*, **16**, 255—267).—See this vol., p. 904.

Estimation of Homogentisic Acid in the Urine. By E. Baumann (*Zeit. physiol. Chem.*, **16**, 268—270).—Mörner (see this vol., p. 904) having proved that it is advisable to use more concentrated ammonia in the estimation of gallic acid in the urine than was previously suggested, the author has found it advisable to modify his method of estimating homogentisic acid in cases of alcaptonuria. The amended method is now as follows:—

10 c.c. of urine is mixed in a flask with 10 c.c. of 3 per cent. ammonia; this is then titrated with decinormal silver nitrate solution; the mixture, after the addition of 5 drops of calcium chloride solution and 10 drops of ammonium carbonate solution, is filtered, and the filtrate tested with silver nitrate; if any reduction occurs, another quantity of urine is similarly treated, only more standard silver solution is employed. This is repeated as often as necessary, excess of silver being recognised by hydrochloric acid. 1 c.c. of the silver solution corresponds with 0·004124 gram of homogentisic acid.

W. D. H.

Assay of Commercial Toluidine. By F. F. Raabe (*Chem. Zeit.*, **15**, 116, 179—180). The author remarks that, in order to prevent as much as possible analytical differences, it will be necessary for the buyers to agree with the manufacturers on a definite method of testing. The process should, however, be such a one as can be readily mastered by anybody who has a sufficiency of the sample at his disposal. In testing toluidine, particular notice must be taken of its appearance, which should be as clear as good ale, although the colour is spoiled to some extent when the sample has been stored in iron barrels. The presence of higher homologues may be ascertained by taking the boiling point. 100 c.c. of the sample is fractioned in a retort holding about 180 c.c., the heat being so regulated that about two drops distil over every second. The specific gravity is best taken by means of Lunge's hydrometer. To get the temperature exactly at 15°, the oil is put into a cylinder, which is then surrounded by another cylinder filled either with warm or, if necessary, with iced water.

These simple tests are, however, hardly sufficient now-a-days, when the buyers demand a specified percentage of paratoluidine. Of the various methods from time to time proposed, the author has most faith in Lorenz's oxalic acid process, which is carried out as follows:—A definite volume of an ethereal solution of dry oxalic acid is added to a known quantity of pure paratoluidine mixed with a few drops of orthotoluidine, and after some time the liquid is filtered off, the ether expelled, and the excess of acid titrated with solution of sodium carbonate, with delicate litmus-paper as indicator. In this way we get a standardised solution of oxalic acid, which may then be used for testing any given sample. The author has tried to estimate the paratoluidine gravimetrically as oxalate by simply adding a large excess of an aqueous solution of oxalic acid, and has obtained very satisfactory results when analysing samples containing from 25 to 40 per cent. of paratoluidine. A process, which he believes to be a very suitable one for daily use by manufacturers, and on which he is still engaged, consists in taking the solidifying point of the sample after first fusing it

with a definite amount of pure dried paratoluidine. The operator must, however, be in possession of a large number of standard mixtures containing, say, 82·5, 83, 83·5, 84, 84·5, and 85 per cent. of pure paratoluidine for comparison. L. de K.

Test for Guanidine. By E. Schulze (*Ber.*, **25**, 661—662).—Many salts of guanidine (the nitrate, sulphate, hydrochloride, and carbonate were examined) give with Nessler's reagent a white or faintly yellowish precipitate, at first flocculent and bulky, but collecting together after a time. The reaction is very delicate; a 0·05 per cent. aqueous solution of guanidine nitrate gives an appreciable precipitate; a 0·01 per cent. solution is rendered turbid. C. F. B.

Assay of Opium. By D. B. Doti (*Pharm. J. Trans.* [3], **51**, 746).—The paper points out some sources of possible error in Teschemacher and Smith's gravimetric process of opium assay, and recommends the following method:—10 grams of the opium in powder is exhausted with spirit (sp. gr. 0·92), one or two drops of ammonium oxalate added, and then ammonia, until the spirit is only slightly acid. The extract is evaporated to one-third, cooled, filtered, the filtrate concentrated to 5 c.c., and transferred to a small flask with the aid of 4 c.c. of water and 3 c.c. of spirit; 2·2 c.c. of aqueous ammonia (sp. gr. 0·96) and 25 c.c. of ether are added. After 18 hours, the precipitate is collected on a tared filter, washed with morphiated water, dried, washed with benzene, dried, weighed, and finally titrated with N/10 sulphuric acid. R. R.

Analysis of Tea. By A. Domergue and C. Nicolas (*J. Pharm.*, **25**, 302—306).—For the estimation of the theïne, 5 grams of coarsely-powdered leaves was boiled some minutes in 50 to 60 c.c. of water. To the boiling liquid is added 100 c.c. of a 3 per cent. solution of mercuric acetate; after boiling a little longer, all is passed into a moistened filter, and washed with hot water, until the washings become colourless. The solution, about 300 c.c., is concentrated to about 20 c.c., and is mixed with 2 grams of calcined magnesia, and 15 grams of powdered glass or calcined and washed quartz. The mixture is completely dried on the water-bath, and is extracted in a Soxhlet apparatus, with a mixture of equal weights of benzene and chloroform. The solution, on evaporation, yields the theïne only very slightly contaminated with a little waxy matter, which may be neglected. To estimate the manganese, the sulphated ash from 2 grams of tea is boiled with 1 gram of lead peroxide, and 5 c.c. of nitric acid, the solution made up to 50 c.c., and the colour compared with typical solutions of titrated permanganate.

Black teas only of ascertained purity were examined. The amount of theïne varies with the commercial value of the sample. The ash may slightly exceed 6 per cent. The green solution of the soluble part passes rapidly through violet-red before losing its colour. The quantity of soluble matter in tea is very variable. The three last samples had probably been previously extracted; the ashes of these three were not green, and, when treated with water, the solutions ob-

Commercial Varieties.	Water per cent.	Ash.					Extract.	Theïne.	Sulphated ash.	Manganese.
		Per cent.	Colour.	Insoluble.	Soluble.	Colour of solution.				
Assam	8·76	5·65	Green.....	1·66	4·00	Wine-red..,	53·85	4·39	..	From 0·022 to 0·065 per cent.
Flowers of Pekoe, 1st .	9·14	5·20	Greenish	1·28	3·92	Rose.....	48·18	4·25	6·45	
„ „ 2nd.	10·70	5·46	Greenish-grey.....	1·86	3·60	„	43·60	3·78	7·05	
Manning Congou.....	9·00	6·14	Greenish-white . .	2·54	3·60	„	45·25	3·20	7·75	
Congou Pekoe, 1st....	10·68	6·34	Greenish	2·54	3·80	„	55·73	2·74	7·75	
Orange „ 1st....	10·80	5·78	Malachite-green ...	2·12	3·66	„	49·03	3·49	7·65	
Extra Souchong, 1st .	9·86	5·40	„ „ ...	2·00	3·40	„	35·10	2·56	6·85	
Pekoe Congou, 2nd...	9·00	5·76	Greenish-grey	2·10	3·66	„	40·60	3·00	7·35	
Extra Souchong, 2nd..	10·60	5·40	Malachite-green ...	2·20	3·20	„	37·55	2·27	7·20	
„ Congou, 1st....	9·22	5·70	Greenish-white....	2·40	3·30	„	38·75	2·75	8·25	
Java Souchong.....	9·74	6·16	Malachite-green...	2·50	3·66	„	39·50	3·00	8·35	
Extra Souchong, 3rd .	11·74	5·80	Grey-green	2·60	3·20	„	31·30	2·73	7·40	
Superior Souchong ..	11·00	5·70	„ „	2·66	3·04	„	29·55	2·72	7·50	
Orange Pekoe, 2nd...	8·60	5·26	Malachite-green ...	2·23	3·00	„	42·55	2·33	7·15	
Superfine Souchong ..	8·96	5·56	Grey-green	2·70	2·86	„	31·00	2·68	7·85	
„ „ ..	9·20	5·66	„ „	2·55	3·11	„	31·40	2·35	8·55	
Fine Souchong.....	8·96	6·18	Rose-grey	4·12	2·06	Colourless ..	29·35	1·20	9·15	
Extra Congou, 2nd ...	9·30	6·28	Blackish-grey	4·32	1·96	„	33·10	1·60	9·10	
Fine Congou	9·34	5·83	„ „	4·02	1·86	„	33·35	0·91	7·90	

tained were colourless. Evidently the manganese is contained in tea in a soluble form; for spent leaves yield a grey ash, which again gives a colourless solution. A black tea may be considered to be bad in quality if it contains less than 2 per cent. of theïne, and gives an ash not green in colour, the aqueous extract of which is colourless, and if the insoluble part of the ash equals or exceeds the soluble.

J. T.

Analysis of Gambier. By H. R. Procter (*J. Soc. Chem. Ind.*, **10**, 681—683).—The author has been in communication with English and Continental chemists interested in the analysis of tanning materials, asking their opinion as to the possibility of agreeing on a standard method for the analysis of gambier, in order to avoid the serious discrepancies which arise in consequence of all the present processes being anything but perfect. His correspondents are unanimously in favour of the indirect gravimetric method, in which equal quantities of the infusion of the tanning material are evaporated, in the one case after careful filtration through paper only, and in the other after complete removal of the tanning matter by treatment with purified hide powder; and the tanning matter is calculated from the difference of weight of the dried residues. There is, however, considerable diversity of opinion as to the details, both of making the infusion and of carrying out the absorption of the tannin, and in the present paper the author has briefly summarised the points still requiring discussion, and the respective advantages of the various modifications, in the hope that some chemists may be induced to make independent investigation where it is required, and communicate with him, so as to enable him to outline at an early date, a method which will represent as nearly as possible the average of chemical opinion.

D. B.

A Sensitive Reaction for Albumin in Urine. By E. Spiegler (*Ber.*, **25**, 375—378).—The urine is acidified with a little concentrated acetic acid, filtered if necessary, and cautiously dropped by a pipette into a test tube half filled with a solution of mercuric chloride (8 parts), tartaric acid (4 parts), and sugar (20 parts), in water (200 parts) in such a manner that the two liquids do not mix; the presence of albumin is indicated by the formation of a white ring at the point of contact of the two liquids. The solution prepared as above described has a sp. gr. 1·06; the sugar plays no part in the reaction, but is merely added to raise the density of the solution, and prevent its mixing with the urine; with dense diabetic urines, a further addition of sugar is needful. The acidification of the urine with acetic acid is necessary to precipitate mucus, and to decompose carbonates and alkali phosphates, which interfere with the reaction; urines which are turbid through bacteria need not be clarified. Several samples of urine, free from albumin, from women after parturition, in which the presence of peptone was indicated by biuret, were found not to give the above-described reaction; propeptone (hæmialbumose), however, does give it. By the new reaction, 1 part of albumin in 225,000 can be detected, whereas the potassium ferrocyanide reaction is only sensitive to 1 part in 50,000.

A. R. L.

General and Physical Chemistry.

Refractive Indices of Saline Solutions. By P. Bary (*Compt. rend.*, **114**, 827—830).—The refractive indices of solutions of various strengths were determined, and the results plotted in curves, the abscissæ representing the quantity of anhydrous salt in 100 parts of the solution, whilst the ordinates represent the refractive indices. The general result is that the curve representing the variation of the refractive index with the concentration of the solution is not continuous, but is made up of several right lines with different inclinations to the axis of the ordinates. Each break indicates a sudden change in the molecular condition of the medium, and most probably corresponds to the formation of a new compound, or, in other words, a new hydrate in the solution. The composition of the solutions at the points where the breaks occur can be represented by molecular formulæ. The following table gives the composition of the solutions and their refractive indices at the breaks :—

Sodium thiosulphate.—$Na_2S_2O_3 + 40H_2O$, 1·3658; $Na_2S_2O_3 + 20H_2O$, 1·3097.

Potassium dichromate.—$K_2Cr_2O_7 + 250H_2O$, 1·3438; $K_2Cr_2O_7 + 170H_2O$, 1·3478.

Potassium chloride.—$KCl + 80H_2O$, 1·3423.

Sodium chloride.—$NaCl + 30H_2O$, 1·3528; $NaCl + 15H_2O$, 1·3686.

Lithium sulphate.—$Li_2SO_4 + 150H_2O$, 1·3415; $Li_2SO_4 + 30H_2O$, 1·3610.

Ferrous sulphate.—$FeSO_4 + 70H_2O$, 1·3570.

Silver nitrate seems to be an exception, but it is possible that the variations are within the limits of the error of experiment, and that the exception is only apparent. C. H. B.

Determination of the Molecular Refraction of Solid Chemical Compounds in Solutions of the same. By F. Schütt (*Zeit. physikal. Chem.*, **9**, 349—377).—Continuing his researches (Abstr., 1890, 1033) on the molecular refraction of solutions, the author has examined the behaviour of mixtures of ethylene bromide and propyl alcohol. The results obtained are, generally speaking, similar to those in the case of sodium chloride solutions.

The discrepancy between the observed and calculated values led the author to a further examination of the formulæ employed in the calculations. The formula used for calculating the molecular refractions of mixtures from those of the components has been hitherto $100K/d = pK_1/d_1 + (100 - p)K_2/d_2$, in which $K = (n - 1)/1$. For this Pulfrich's formula may be substituted,

$$K\frac{1 - aC}{1 - C} = v_1K_1 + v_2K_2,$$

where C is the contraction which takes place on mixing the volumes v_1 and v_2 of the two solutions and α is a variable factor. This last quantity the author finds is proportional to the percentage composition $a = \alpha + \beta p$, and therefore the above formula becomes

$$K = \left(\frac{v_1}{v} K_1 + \frac{v_2}{v} K_2\right) \frac{1}{1 - C(\alpha + \beta p)},$$

where $v = 1/(1 - C)$. The author finds that results calculated with this formula show a most excellent agreement with those obtained by observation, both in the case of the sodium chloride solutions and the mixtures of ethylene bromide and propyl alcohol. To determine the molecular refraction of a solid or liquid substance from those of its solutions, since $K/d = R$, $K_1/d_1 = R_1$, and $K_2/d_2 = R_2$,

$$R_1 = R\left[\frac{1 - C(\alpha + \beta p)}{1 - C}\right]\frac{100}{p} - R_2\frac{100 - p}{p}.$$

The molecular refraction of solid sodium chloride can be calculated to within the third decimal place of the observed value, from solutions containing even less than 1 per cent. of the salt, with the aid of this formula. H. C.

Spectra of Gallium. By L. de Boisbaudran (*Compt. rend.*, **114**, 815—818).—When the non-condensed spark from a coil with a long wire is allowed to impinge on the surface of a solution of gallium chloride, the spectrum consists of a band at λ 509·04—λ 495·50, with a maximum at λ 502·33, a strong, narrow band at 417·04, and a well-marked narrow band at 403·19. If the coil is connected with a condenser, or if the spark passes between poles of metallic gallium, a more complex spectrum is obtained, although the band with a maximum at λ 502·33 is no longer visible. Bands are observed at 645·27, 641·24, 639·23, 632·67, 599·49, 585·15, 580·14, 542·89, 536·95, 533·97, 521·26, 499·33, 486·46, 438·22, 425·58, 417·04, 403·19. A Demarcay coil with a short wire gives a spectrum very different in the number and relative intensities of the lines. Bands are seen at 641·24, 639·23, 632·67, 535·51, 417·04, 403·19. The remarkable variations in the spectrum of gallium caused by variations in the nature of the spark illustrate the great importance of defining precisely the conditions under which electric spectra are obtained. C. H. B.

Changes of E.M.F., Volume, and Temperature by Mixing Electrolytes. By G. Gore (*Chem. News*, **65**, 145—147).—In a former communication (this vol., p. 257), the author has shown the effects of dilution on the temperature and total volume of liquids and on the mean amount of E.M.F. of a voltaic couple immersed in them; he has now examined in a similar manner the effects of mixing electrolytes on the same phenomena, and in order to obtain some new information respecting the chemical substitution of acids and the double decomposition of salts, pairs termed "isomeric mixtures" were employed, and were divided into two groups, acids + acids and salts + salts. The equivalent weight of each substance in grains

being dissolved in 1800 grains of water, the various data were recorded before and after admixture in the manner described in the previous paper.

With regard to the changes of mean E.M.F., total volume, and temperature attending the expulsion of one acid from a salt by means of another acid; in 15 isomeric couples of mixed liquids every mixture suffered a change of either one or all of these during the mixing, but in every instance each of the two mixtures of an isomeric couple gave the same amount of E.M.F., demonstrating that whatever change took place during the mixing, the final result was the same; in fact, a counter-balancing of forces appears to take place. With regard to the question of substitution of one acid by another, as exemplified by these experiments, sulphuric is observed to expel nitric, hydrochloric, and acetic; whilst hydrochloric expels nitric and hydrobromic more readily than the reverse. With mixtures of salts, changes were observed, as in the above experiments, during mixing, but the amount of E.M.F. produced in duplicate mixtures was the same; the three series of changes of volume, temperature, and E.M.F. in these cases largely agree with each other, but the agreement is generally less distinct than with the series of mixtures of acids + salts. Generalising on the results obtained in these investigations, it is pointed out that whenever admixture produces an increase of velocity and freedom of molecular motion there is a proportional gain in the mean E.M.F. and *vice versâ*; this considered in conjunction with the distinct connection also exhibited between changes of total volume, total heat, and mean amount of E.M.F., helps to confirm the existence of a mechanical basis of voltaic and chemical action.

D. A. L.

Correction in the Calculation of the Heat of Dissociation of Electrolytes. By S. Arrhenius (*Zeit. physikal. Chem.*, **9**, 339—342).—Van der Waals (Abstr., 1891, 1309), Nernst, Jahn, and Trevor have all pointed out an error which occurs in the author's calculation of the heat of dissociation of electrolytes. In this paper the necessary correction is made, and the heats of dissociation of a number of electrolytes recalculated. H. C.

Persulphuric Acid and its Salts. By Berthelot (*Compt. rend.*, **114**, 875—883).—The author prepared potassium and ammonium persulphates by Marshall's method (Trans., 1891, 772) but placed the sulphate solution inside the porous cell, and used a platinum wire as the anode. He states that, under these conditions, the yield is greater than when the anode has a large surface. The potassium or ammonium sulphate is dissolved in sulphuric acid diluted with six to eight times its volume of water. Barium persulphate is obtained by adding barium hydroxide to a solution of the ammonium salt, expelling the ammonia at the ordinary temperature in a vacuum, and precipitating excess of barium by carbonic anhydride.

Heat of dissolution,		$K_2S_2O_8$ at 9·7°	−14·36 Cal.
,,	,,	$K_2S_2O_8$ at 5·6°	−15·34 ,,
,,	,,	$(NH_4)_2S_2O_8$ at 10·5°....	− 9·72 ,,
,,	,,	$BaS_2O_8 + 4H_2O$ at 12° ..	−11·80 ,,

The heat of neutralisation was determined by precipitating the barium salt with dilute sulphuric acid; the value per equivalent is +13·8 Cal., identical with the heat of neutralisation of thiosulphuric, nitric, and hydrochloric acids. The heat of neutralisation with potassium or sodium hydroxide is +13·7 Cal., and with ammonia +12·4 Cal. Sulphuric acid does not completely displace persulphuric acid from its salts, but a condition of equilibrium is established.

In order to measure the heat of formation of persulphuric acid, the heat developed by the action of persulphates in presence of sulphuric acid on ferrous sulphate was compared with the heat developed by the action of hydrogen peroxide on the same reducing agent under similar conditions, matters being so arranged that the final composition of the solution was the same in both cases. As a mean result, the reduction of persulphuric acid was found to develop +13·2 Cal. more than the reduction of hydrogen peroxide. From this result the following values can be calculated:—

S_2 (octahedra) + O_8 + H_2 + water = $H_2S_2O_8$ dil.	develops	+316·2 Cal.
$S_2 + O_7 + H_2O$ + water = $H_2S_2O_8$ dil.	,,	+247·2 ,,
$K_2S_2O_8 + H_2O = SO_4H_2$ dil. + K_2SO_4 diss. + O	,,	+ 36·3 ,,
$K_2S_2O_8$ sol. + H_2O sol. = $2KHSO_4$ sol. + O	,,	+ 28·1 ,,
$K_2S_2O_8$ sol. + $K_2S_2O_7$ + O	,,	+ 19·5 ,,
$K_2 + S_2 + O_8$ + water = $K_2S_2O_8$ diss.	,,	+453·6 ,,
$K_2 + S_2 + O_8 = K_2S_2O_8$ sol.	,,	+439·2 ,,
$(NH_4)_2S_2O_8$ diss. + $H_2O = H_2SO_4$ dil. + $2NH_4HSO_4$ diss. + O	,,	+ 37·1 ,,
$(NH_4)_2S_2O_8$ sol. + H_2O sol. = $2NH_4HSO_4$ sol. + O	,,	+ 27·0 ,,
$N_2 + H_8 + S_2 + O_8$ + water = $(NH_4)_2S_2O_8$ diss.	,,	+383·0 ,,
$N_2 + H_8 + S_2 + O_8 = (NH_4)_2S_2O_8$ sol.	,,	+392·7 ,,
$BaS_2O_8 + H_2O = BaSO_4$ ppt. + H_2SO_4 dil. + O	,,	+ 44·2 ,,

The difference between the heats of formation of potassium and ammonium persulphates from their elements is the same as the difference in the case of the sulphates.

The fact that barium persulphate decomposes more readily than the alkaline salts is explained by the fact that the liberation of heat accompanying the change is greater in the first case. The anhydrous potassium salt undergoes practically no alteration when kept; the hydrated barium salt gradually decomposes into sulphate and sulphuric acid.

The formation of persulphuric acid and the persulphates from free oxygen and sulphuric acid or sulphates is endothermic, but the necessary energy may be supplied by the electric current, the heat of hydration of strong sulphuric acid, &c. The author has previously observed that persulphuric acid is formed by the action of hydrogen

peroxide on concentrated sulphuric acid. If too much water is present, the sulphuric acid combines with it in preference to acting on the hydrogen peroxide; if the sulphuric acid is too concentrated, it decomposes the persulphuric acid.

When barium peroxide is added to well-cooled concentrated sulphuric acid, persulphuric acid is formed, but if the addition of the peroxide is continued, at a certain point the mixture evolves a quantity of thick vapour, with a strong odour, and all the persulphuric acid decomposes, probably because it has passed the maximum concentration consistent with stability. C. H. B.

Sugars. By J. Fogh (*Compt. rend.*, **114**, 920—922).—

	Heat of combustion, 1 gram.	Heat of combustion, 1 molecule.		Heat of formation.
		Constant volume.	Constant pressure.	
	Cal.	Cal.	Cal.	Cal.
Glucoheptite, $C_7H_{16}O_7$	3966·5	840·9	841·2	370·9
Glucoheptose, $C_7H_{14}O_7$	3732·8	783·9	783·9	359·2
Glucoheptonic lactone, $C_7H_{12}O_7$	3494·8	726·9	726·6	347·5
Glucooctonic lactone, $C_8H_{14}O_8$	3518·7	837·5	837·2	400·2
Dextromannonic lactone, $C_6H_{10}O_6$	3477·8	619·0	618·7	292·1
Lævomannonic lactone, $C_6H_{10}O_6$	3465·7	616·9	616·6	294·2
Lævogulonic lactone, $C_6H_{10}O_6$	3456·8	615·3	615·0	295·8
Allomucic acid, $C_6H_{10}O_8$	2358·8	495·3	494·5	416·3
Inactive trihydroxyglutaric acid, $C_5H_8O_7$	2163·7	389·5	388·7	358·2

In the first three, which represent an alcohol, an aldehyde, and a dehydrated monobasic acid, the heat of formation diminishes regularly by 11·7 Cal., in consequence of the successive loss of CH_2.

C. H. B.

Thermochemistry of Hydrazine and Molecular Refraction of some Nitrogen Compounds. By R. Bach (*Zeit. physikal. Chem.*, **9**, 241—263).—The author has obtained the following thermochemical data with regard to some of the derivatives of hydrazine and azoimide:—

$N_2H_5{\cdot}OH + Aq = N_2H_5{\cdot}OH,Aq$ ..... + 19·19 Cal.
$N_2H_5{\cdot}HSO_4 + Aq = N_2H_5{\cdot}HSO_4,Aq$ ..... − 85·27 ,,
$N_2H_5Cl + Aq = N_2H_5Cl,Aq$ ..... − 54·40 ,,
$N_2H_5Cl,HCl + Aq = N_2H_5Cl,HCl,Aq$ ..... − 62·01 ,,
$NH_3,N_3H + Aq = NH_3,N_3H,Aq$ ..... + 67·34 ,,
$H_2SO_4,Aq + N_2H_5{\cdot}OH,Aq = N_2H_5{\cdot}HSO_4,Aq.$ +113·0 ,,
$2HCl,Aq + N_2H_5{\cdot}OH,Aq = N_2H_5Cl,HCl,Aq$ + 96·0 ,,
$HCl,Aq + N_2H_5{\cdot}OH,Aq = N_2H_5Cl,Aq$..... + 96·5 ,,
$2HNO_3,Aq + N_2H_5{\cdot}OH,Aq = N_2H_4,2HNO_3,Aq$ + 97·0 ,,
$HNO_3,Aq + N_2H_5{\cdot}OH,Aq = N_2H_5{\cdot}NO_3,Aq$.. + 97·0 ,,
$NH_3,Aq + N_3H,Aq = NH_4{\cdot}N_3,Aq$..... + 83·0 ,,

The heat of formation of hydrazine hydrate was determined by oxidising the hydrate with chromic acid, and also by decomposing it with an ammoniacal solution of silver nitrate. The first method gave for the heat of formation of the hydrate in solution 561 Cal., the second method gave the value 663 Cal. The author regards the latter value as the more probable, and from this the heat of formation of the anhydrous hydrate may be deduced.

$$N_2 + H_6 + O = N_2H_5{\cdot}OH \ldots\ldots\ldots \quad +644 \text{ Cal.}$$

The fact that the heat of formation is a positive quantity shows that hydrazine hydrate is not the analogue of the diazo-compounds. It therefore probably has the constitution $H_2N{\cdot}NH_3{\cdot}OH$, and not $H_3N{:}NH_2{\cdot}OH$.

It appears from the above table that the hydrazine salts $N_2H_4{,}HR$ are not converted into $N_2H_4{,}2HR$ salts in aqueous solution, as the heats of neutralisation of hydrazine hydrate by either one or two equivalents of the acid are the same. From this, it is probable that the salts $N_2H_4{,}2HR$ undergo hydrolytic dissociation in aqueous solution, and this, taken in conjunction with the electrolytic dissociation which takes place at the same time, would explain the fact that the molecular weights of these salts determined by the cryoscopic method are only one-fourth of those expressed by their formulæ (Abstr., 1891, 264).

The determination of the molecular refraction of hydrazine hydrate and some of its salts led to the unexpected result that the atomic refraction of nitrogen deduced from the molecular refraction of the hydrate is much smaller than the value obtained from the other hydrazine salts and other nitrogen compounds. The value for the two nitrogen atoms calculated for the formula $(n-1)/d$ is 9·5 in the case of the hydrate, and nearly 11 for the salts. In this behaviour, hydrazine resembles ammonia, as the latter in aqueous solution also gives a very much smaller value for the atomic refraction of nitrogen than that deduced from the ammonium salts or the amines.

H. C.

Determination of Vapour Density. By C. Schall (*Ber.*, **25**, 1490—1491).—A supplementary note to the previous papers on this subject (compare Abstr., 1890, 681, 1042). It is desirable to calculate the smallest quantity of substance which may be used for each determination, so as to secure the greatest possible accuracy.

J. B. T.

Determination of the Density of Liquefied Gases and of their Saturated Vapours. By E. H. Amagat (*Compt. rend.*, **114**, 1093—1098).—The method proposed for determining the density of liquefied gases and their saturated vapours is the following:—Starting with the gas, a portion of this, say one-tenth of its volume, is liquefied, and the volumes of liquid and vapour carefully determined. A further portion of the gas is then liquefied, so that the volume of the liquid may be three or four times increased, and the volume again determined. If ΔV and $\Delta V'$ represent the increase in the volume of the liquid and the decrease in the volume of gas, and D and D′ are the densities of the liquid and the gas, $\Delta V/\Delta V' = D'/D$. On the other

hand, if V and V′ be taken to represent the volumes of gas and liquid in one of the above experiments, VD + V′D′ = P, the weight of material used. From these equations, the values of D and D′ can be deduced.

The difficulty of making determinations by the above method increases as the critical point is approached. The author has, however, applied the method with success in the case of carbonic anhydride, even up to the critical point, at which the densities of liquid and vapour become the same. A table is given for the values of the densities of liquid carbonic anhydride and its saturated vapour for each degree from 0° to the critical point. H. C.

Liquid and Gaseous Mixtures. By J. A. Wanklyn (*Chem. News*, **65**, 122—123; compare Abstr., 1891, 1412, and this vol., p. 264).—In more recent experiments on the specific gravity of sugar solutions, the author and his collaborators, working with larger quantities ($\frac{1}{2}$ litres) of solution, find that the increment coefficient of cane sugar is 0·388, instead of 0·371, and is constant for solutions containing 1 gram, and up to as much as, and probably even more than, 105 grams per litre, but this number falls in very strong and viscid solutions, containing, for instance, 749·5 grams per litre; this is assumed as due to solution in these being imperfect, and to a physical variation in the condition of the sugar, by which its specific gravity approximates to 1·606, that of solid sugar, instead of to 1·634, the sp. gr. of fluid sugar in the more mobile solutions. Saline solutions are also regarded as mixtures of fluid hydrates with water, in which no change of volume of any kind obtains, and these investigators are of opinion that the volumes of either gaseous or liquid mixtures is equal to the sum of the volumes of the constituents separately measured. D. A. L.

Theory of Diffusion and Electrolysis. By M. Planck (*Zeit. physikal. Chem.*, **9**, 347—348).—The author shows that Wiedeburg's statement (*Zeit. physikal. Chem.*, **9**, 143) of an error in the theory of hydrodiffusion developed by himself and Nernst rests upon a mistaken assumption. H. C.

Applicability of Planck's Proof of the Law of Van't Hoff. By S. Arrhenius (*Zeit. physikal. Chem.*, **9**, 330—334).—The author raises some objections to recent observations of Planck with regard to the application of gaseous laws to dilute solutions, firstly on the ground of priority, and secondly with the view of showing that Van't Hoff's law cannot, as Planck maintains, be deduced *a priori* and without other assumptions from the laws of thermodynamics. H. C.

Determination of the Freezing Point of very Dilute Aqueous Solutions. By F. M. Raoult (*Zeit. physikal. Chem.*, **9**, 343—346).—The author has improved the apparatus which he formerly employed for the determination of the freezing points of solutions. The beaker containing the solution is immersed in a 40 per cent. glycerol solution, which is kept in constant motion and cooled by means of a copper worm tube, through which water at a temperature about 3°

below the freezing point of the solution under examination circulates. The thermometer used for taking the observations acts as the stirrer, as a network of platinum is situated round the bulb and attached to the stem, and the whole is rapidly rotated before taking an observation. With this apparatus, the freezing point of distilled water is found to correspond with the melting point of ice to within 1/500 of a degree.

The author has redetermined the freezing points of cane sugar solutions, and finds, in accordance with his former determinations, that the molecular reduction increases with increasing dilution when a certain limit is reached (this vol., p. 678). H. C.

Action at a Distance of Aqueous Solutions on Water Vapour. By M. W. Beyerinck (*Zeit. physikal. Chem.*, **9**, 264—266).—The author has observed that a drop of an aqueous solution placed upon a glass plate has the power of absorbing water vapour from its immediate neighbourhood, and thus surrounding itself with a sphere which is apparently free from moisture. The size of this sphere varies considerably with the nature of the solution taken, probably depending on its surface tension, and the method might, perhaps, be made available for determining the vapour pressures of aqueous solutions. H. C.

Velocity of Reaction in Mixtures of Isohydric and Non-isohydric Solutions of Acids. By B. Moore (*Zeit. physikal. Chem.*, **9**, 327—329).—Isohydric solutions of acids contain hydrogen ions in equal concentration, and Arrhenius has shown (Abstr., 1887, 415) that when such solutions are mixed the concentration remains unaltered. If in two acid solutions the concentration of the hydrogen ions is not equal, the one solution will influence the degree of dissociation of the other, in such a manner that the concentration of the ions in the mixture is not the arithmetical mean of the concentrations in each solution. From this it follows that mixtures of non-isohydric solutions will bring about reactions with a velocity which is not the mean velocity of their components. In order to test this view, methyl acetate was hydrolysed by isohydric and non-isohydric solutions of hydrochloric, and di- and trichloracetic acids, and the velocity of the different reactions measured. The results obtained were in perfect accordance with the general theory. H. C.

Labile Conditions of Equilibrium in Mixtures of Two Substances at a Temperature below the Melting Point of either. By A. Blümcke (*Zeit. physikal. Chem.*, **9**, 323—326).—The object of the experiments described in this paper was to test some of the theoretical conclusions which have been arrived at in former communications (Abstr., 1891, 375; this vol., p. 259). With mixtures of sodium thiosulphate with potassium nitrate, of sodium acetate with potassium nitrate, and also of sodium thiosulphate with acetate, it has been found possible to obtain labile conditions of equilibrium below the melting points of either substance. The experiments are only of a qualitative character, but serve, as far as they can at present be extended, to

confirm the author's conclusions with respect to the isothermals of mixtures of two substances. H. C.

Equilibrium of Chemical Systems under Unequal Pressures. By H. Le Chatelier (*Zeit. physikal. Chem.*, **9**, 335—338).—The case is considered of a solid substance in contact with either a liquid or a gas being brought under a different pressure. If this takes place without chemical change, then the sum of the chemical energy expended during the alteration of the pressure or temperature must be zero. If L is the latent heat of the reaction and N the latent work of each different element in the system which accompanies the volume change v, p the pressure, and t the absolute temperature, $L\,dt/t + \Sigma N dp/p = 0$. The formula is applied with satisfactory results to some of the changes of water in contact with ice.

H. C.

Influence of Foreign Substances on the Form, Purity, and Size of Crystals separating from a Solution. By J. W. Retgers (*Zeit. physikal. Chem.*, **9**, 267—322).—The author points out that very little is at present known with regard to the conditions which determine the form, purity, and size of crystals separating from a solution. The form is often influenced in a totally unexplained manner by the presence of a foreign substance in the solution from which the crystals are separating. Thus, ordinary salt, which usually crystallises in cubes, will separate out in octahedra from a solution which contains urea. This may be due to the difference in physical character of the cube and octahedron faces, this difference inducing a difference in the capillary attraction between the faces and the different solutions into which the crystal may be introduced, so that in one case the attraction may be greater for the cube, in the other greater for the octahedron faces, and thus the growth of the one or the other favoured as the case may be. The purity of crystals is subject to similar unexplained influences. Lead nitrate can only be obtained in opaque crystals from a pure, aqueous solution, but in the presence of free nitric acid the crystals which separate are perfectly clear and transparent. With regard to the size, the author believes that there is a distinct maximum limit of size for every crystal, beyond which the crystal is incapable of further growth. The maximum varies with the same crystal, somewhat, with the bulk of the solution from which it is crystallised, but there is a particular maximum limit when the bulk of the solution ceases to exercise any influence. Crystals of alum and magnesium sulphate, which had apparently reached such a maximum size, have been kept for days in strongly supersaturated solutions without undergoing the least change, although the solutions, when disturbed, gave copious separations of smaller crystals. This maximum in size is also, in certain cases, influenced by the presence of foreign substances, salt crystals being obtained of larger size from solutions containing cupric chloride than from pure aqueous solutions.

In order to obtain some further evidence on the above points, the author has examined crystals of the different haloïd salts of the alkali metals and ammonium, obtained from solutions containing a

number of foreign impurities. The chief results with regard to the influence of these impurities on the form of the crystals are given in the following table :—

Salt.	From water.	With urea.	With $CrCl_3$.	With $FeCl_3$.	With $PbCl_2$.
NaCl	Cubic	Octahedral	Octahedral	Cubic	Cubic
KCl	,,	Cubo-octahedral	Cubic	,,	Octahedral
KBr	,,	Cubic	,,	,,	,,
KI	,,	,,	,,	,,	,,
NH_4Cl ...	Trapezoidal	,,	,,	,,	Trapezoidal
NH_4Br ...	,,	,,	,,	Trapezoidal	Cubic
NH_4I	Cubic	,,	Octahedral	Octahedral	Octahedral

H. C.

Relations between Atomic Weights. By H. Adkins (*Chem. News*, **65**, 123—124).—It is shown that numbers representing all the atomic weights may be obtained by additive combinations of the numbers 7, 9, 11, and 12, being the atomic weights of lithium, glucinum, boron, and carbon respectively. D. A. L.

Inorganic Chemistry.

Slow Combustion of Gaseous Mixtures. By P. Askenasy and V. Meyer (*Annalen*, **269**, 49—72).—The authors have continued the experiments, commenced by Krause and Meyer (Abstr., 1891, 1153), on the rate of combination of oxygen and hydrogen, in order to try and ascertain the cause of the irregularity of the previous results, and, if possible, to get rid of all disturbing influences, so that the relation between time and amount of water formed could be determined.

The electrolytic gas was prepared as already described, and purified with the greatest care ; in addition to the precautions previously observed, it was passed through a glass tube, heated to 518° in the vapour of phosphorus pentasulphide, in order to ensure the decomposition of any ozone or hydrogen peroxide which might be present, then through solutions of potassium iodide (from which, however, no liberation of iodine took place) and concentrated potash and finally dried with concentrated sulphuric acid.

In some preliminary experiments, the electrolytic gas was passed through potassium permanganate in order to free it from hydrogen peroxide ; it was found, however, that the potassium permanganate was reduced by the hydrogen in the mixture, and, also, that absolutely pure hydrogen is completely absorbed by potassium permanganate with formation of a brown precipitate (compare Wanklyn and Cooper, *Phil. Mag.* [5], **6**, 288, and Jones, Trans., 1878, 95).

When electrolytic gas, purified in the manner described, is passed at a moderate rate for 10 hours through a glass tube heated to 518°, only a very small quantity of water (0·7—1·7 milligrams) is produced (compare Meyer, this vol., p. 562); when the glass tube is heated to 606°, a somewhat larger quantity of water is formed, but only a very small proportion of the two gases enter into combination.

The authors then describe in detail a number of experiments which were made in order to determine the amount of water formed on heating electrolytic gas in glass bulbs at 518° for two hours; although various devices were adopted, such as etching the inside of the bulbs, protecting the bulbs from the light, passing electrolytic gas for many hours through the bulbs heated at 518°, in order to obtain an unchangeable surface previous to their employment in the quantitative experiments, constant results could not be obtained. The effect of coating the inner surfaces of the bulbs with silver has been already referred to by Meyer (*loc. cit.*); further experiments have shown that when such silvered bulbs are employed, and the heating is continued for two hours, complete combination takes place at temperatures above 218°; at 183° about 70 per cent. of the electrolytic gas is converted into water, but at 155° only a comparatively very small quantity of water is formed, and at 100° no appreciable combination takes place, even after heating for four hours. The quantity of water produced on heating pure electrolytic gas in the silvered bulbs for two hours at 183° was just as variable as in the experiments with unsilvered vessels.

The conclusion to be drawn from this investigation is, that it is impossible to establish any relation between the quantity of water produced on heating electrolytic gas and the duration of the experiment, even when every imaginable precaution is taken to ensure equality of conditions, and this, probably, owing to the irregular action of the surface of the containing vessels; further experiments on the subject are in progress. F. S. K.

Photochemical Notes. By P. Askenasy and V. Meyer (*Annalen*, **269**, 72—73; compare preceding abstract).—Pure, dry electrolytic gas underwent no change when it was exposed to direct sunlight from May to October, in sealed glass bulbs; on opening the bulbs under water, no change in the original volume of the gas was observed. Even when moist electrolytic gas was exposed to the concentrated light of a July sun, and at the same time heated to 606°, no explosion occurred.

Chlorine and hydrogen, both of which had been separately exposed for three to four hours to bright sunlight, did not combine when mixed together in the dark immediately afterwards; this conclusion confirms that previously come to by Bunsen and Roscoe, and proves that Draper's statement to the contrary is untrue. F. S. K.

Preparation of Nitric Oxide. By F. Emich (*Monatsh.*, **13**, 73—77).—In order to obtain this gas in a very pure condition, the author employs the reaction which obtains in a Lunge's nitrometer, namely, treating mercury with a mixture of sulphuric acid and nitric acid.

The purity of the gas was placed beyond question by the results obtained on leading it over glowing copper; the increase in weight of the metal giving the weight of oxygen, whilst the gas evolved, which was collected and measured, gave the weight of nitrogen. In the reaction between copper and nitric oxide, which is attended by the liberation of much heat, the metal is quantitatively converted into cuprous oxide. G. T. M.

Behaviour of Nitric Oxide at High Temperatures. By F. Emich (*Monatsh.*, **13**, 78—85).—According to Gay-Lussac (Gmelin-Kraut's *Handbuch*, **1**, **2**, 452), nitric oxide is resolved into nitrogen and nitrous oxide when passed over glowing platinum; whilst Berthelot (*Compt. rend.*, **77**, 1448) states that, besides these gases, free oxygen is also formed. The author has further investigated this question, and finds that ruddy fumes are produced when the gas, which has been previously passed through a porcelain or platinum tube heated to the highest temperature obtainable in a Fletcher tube-oven, is allowed to come into contact with the air. When, however, the gas is submitted to the very high temperature obtained by the electrical ignition of nets of platinum, platinum-iridium, platinum-rhodium, and palladium wire, it is completely decomposed into nitrogen and oxygen.

The author also finds that, contrary to the statement of Calberla (*J. pr. Chem.*, **104**, 232), silver at a bright red heat exercises no specific action on nitric oxide. He has exactly repeated the experiments made by that author, but in every case considerable quantities of the oxides of nitrogen could be recognised in the escaping gas.

G. T. M.

Reaction between Nitric Oxide and Oxygen. By F. Emich (*Monatsh.*, **13**, 86—89).—The author finds that these gases, in a state of perfect purity and carefully dried by long-continued exposure to phosphorus pentoxide, when mixed, rapidly react, with the production of brown fumes. This observation refutes Traube's tenet, "that no substance, when in a perfectly dry state, unites directly with oxygen" (compare *Ber.*, **18**, 1881). G. T. M.

Action of Potassium Hydroxide on Nitric Oxide. By F. Emich (*Monatsh.*, **13**, 90—97).—Gay-Lussac found (Gmelin-Kraut's *Handbuch*, **1**, **2**, 454) that when nitric oxide is allowed to remain over potassium hydroxide for some months, a diminution in volume of about 75 per cent. occurs, and the residual gas is nitrous oxide, whilst potassium nitrite is present in the solution. Russell and Lepraik (this Journal, 1877, ii, 37) further studied the interaction between the two substances. They allowed them to remain together for 11—12 months, whereby a condensation of 75 per cent. occurred, and observed that when the compounds reacted at 100°, the residual gas contained nitric oxide (1·5 to 2·5 per cent.) and nitrogen (6·5 to 15·1 per cent.) as well as nitrous oxide. The author has investigated the behaviour of nitric oxide with anhydrous potassium hydroxide at a higher temperature (125°), and finds that, under the circumstances, a diminution occurs of 83·3 per cent. in the volume of the gas, which,

after the action, appears to consist entirely of nitrogen. This volume corresponds with the equation $6NO + 4KOH = N_2 + 4KNO_2 + 2H_2O$.

G. T. M.

Manufacture of Nitric Acid. By C. W. Volney (*Chem. Centr.*, 1892, i, 348—349; from *J. Amer. Chem. Soc.*, **13**, 246—251).—The author explains the sudden frothing which frequently takes place when nitric acid is prepared from sodium nitrate and sulphuric acid on the assumption that the first portions pass over at 84°, and that the heating must be commenced cautiously, and the temperature only allowed to rise after the first reaction abates. After the temperature has risen above 109°, no acid passes over until the temperature 117° is reached, when the last portions pass over. The latter acid has a sp. gr. 1·42, and corresponds with the hydrate, $2HNO_3 + H_2O$, which distils at 120—121°, without decomposition.

J. W. L.

Crystallised Anhydrous Sulphates. By P. Klobb (*Compt. rend.*, **114**, 836—838).—When nickel, cobalt, zinc, and copper sulphates are mixed with excess of ammonium sulphate and carefully heated, out of contact with flame gases in a partially covered crucible, until the whole of the ammonium sulphate is volatilised, care being taken not to decompose the metallic sulphate, the anhydrous sulphates remain in a distinctly crystallised condition. Zinc sulphate forms colourless, elongated, and truncated octahedra, rapidly soluble in warm water. Copper sulphate forms grey, slender, prismatic needles, easily soluble in water, especially if hot. Cobalt sulphate forms purplish-red, truncated octahedra, very stable in air, and only slowly dissolved by boiling water. Nickel sulphate forms yellowish-green octahedra, soluble, with difficulty, in boiling water.

C. H. B.

Colloïdal Silver. By E. A. Schneider (*Ber.*, **25**, 1440—1448; compare this vol., p. 775).—The fact that hydrochloric acid precipitates a mixture of silver chloride and silver from colloïdal silver solutions may be explained by supposing either that the solution contains small quantities of oxygen compounds of silver, or that the silver decomposes the hydrogen chloride with formation of silver chloride and hydrogen. On evaporating a very pure colloïdal silver solution to dryness, and heating the residue to redness, only a negligible quantity of oxygen was obtained, showing, with certainty, that no oxygen compounds of silver were present in the colloïdal solution. If silver chloride and hydrogen are formed on treatment with hydrochloric acid, the hydrogen must be occluded by the silver, as no gas escapes, and, on electrolysis in a properly arranged apparatus, it would be expected to reveal its presence by the effect of the polarisation current on the E.M.F. of the solution. From such measurements the author concludes that the silver particles contain occluded hydrogen, which they slowly lose. The quantity of hydrogen present must, however, be very small, no appreciable liberation of gas being observed on amalgamation with mercury under water. The deficiency in the quantity of hydrogen produced, as indicated by the equation $Ag + HCl = AgCl + H$, may be assigned to various causes.

Colloïdal silver solutions always contain a certain amount of ferric salts, and, on adding hydrochloric acid, the following reaction occurs:—$Ag + FeCl_3 = AgCl + FeCl_2$; the proportion of silver chloride present is thus increased. Oxygen is also dissolved in the solution, and, of course, combines with part of the hydrogen liberated. Hydrogen is also required to produce the silver subchloride, Ag_2Cl, which is formed. The presence of small quantities of easily reducible substances, such as citric acid, and the solubility of hydrogen in the solution are sufficient to account for the remainder of the missing hydrogen. W. J. P.

Decomposition of Silver Permanganate. By A. Gorgeu (*Compt. rend.*, **114**, 912—915).—Silver permanganate decomposes slowly at the ordinary temperature, rapidly at 100°, or in hot water, and very rapidly at 135°. The black product, obtained by decomposition in water at 75°, the permanganate being always in excess, has the composition—

MnO.	O (active).	Ag_2O.	O (inactive).	H_2O.	Loss.
32·71	7·33	53·38	2·75	3·29	0·54

The active oxygen is present exactly in the proportion required to form manganite. The quantity of inactive oxygen does not vary with the method of analysis. No similar excess of inactive oxygen is found in other combinations of silver oxide with higher oxides of manganese, but it occurs in the deposit formed on the positive pole during the electrolysis of silver nitrate. This inactive oxygen seems to be united with the silver, but its exact condition has yet to be determined; it seems to exist neither in occlusion nor in true combination. C. H. B.

Occlusion of Hydrogen by Lead. By J. Shields (*Chem. News*, **65**, 195—197).—Bellati and Lussana's method for showing the diffusion of hydrogen through an iron plate, and also Helmholtz and Root's method of showing the occlusion of hydrogen by platinum, when applied to show the occlusion of hydrogen by lead, gave negative results. It is pointed out, moreover, that even Neumann and Streintz's most recent results (this vol., p. 567) can scarcely be regarded as proving the occlusion of hydrogen by lead, considering that the amount of absorption shown by them amounts only to about 0·13 of its volume. D. A. L.

Behaviour of Copper and of the Noble Metals towards some Gases and Vapours. By G. Neumann (*Monatsh.*, **13**, 40—48; compare Neumann and Streintz, this vol., p. 567).—According to Thudichum and Hake (this Journal, 1876, ii, 251), the hydrogen which is retained in copper reduced from the oxide may be perfectly removed by passing over the glowing metal, for some time, a stream of carbonic anhydride. The author finds, however, that the carbonic anhydride does not remove all the hydrogen, and that the process has a further disadvantage, inasmuch as the carbonic anhydride itself, or carbon obtained from it, may be absorbed by the copper. In one

set of experiments, a coil of copper gauze, weighing 29 grams, was found to give, on combustion, from 0·00114 to 0·0079 gram of water, and from 0·0055 to 0·0196 gram of carbonic anhydride. Copper gauze which has been reduced by means of methyl and ethyl alcohols, or by coal gas, and dried at 220°, always retains carbonic anhydride and water; but in quantity so small that the effect produced is usually within the limits of experimental error.

At a temperature of 450°, silver gauze was found to absorb 4·09 to 5·43 times its volume of oxygen, whilst, at the same temperature, gold absorbed from 32·78 to 48·49 times, and platinum from 63 to 77 times respectively their volume of the gas. Palladium, at 450°, is converted into the suboxide Pd_2O.

In the above-described experiments, the temperature was controlled by employing such conditions that zinc (m. p. 412—433°) melted easily, and antimony (m. p. 432—450°) only just melted.

G. T. M.

Aluminium Sulphide. By H. N. Warren (*Chem. News*, **65**, 135—136).—Pure alumina, prepared by dissolving the metal in hydrochloric acid and drying and igniting the product, when exposed, at a full red heat, to a current of carbon bisulphide vapour, neither fuses nor does it yield any aluminium sulphide. But alumina prepared from alum under similar treatment yields, as usually asserted, a glassy mass, evolving hydrogen sulphide when thrown into water; but the author finds the source of both this gas and the glassy appearance is not aluminium sulphide, but a small quantity of potassium sulphide derived from potassium sulphate retained by the alumina. Aluminium sulphide is obtained when aluminium is subjected, at a red heat, to the action of sulphur vapour. D. A. L.

New Iron Salts. By Lachaud and C. Lepierre (*Compt. rend.*, **114**, 915—918).—When ferrous sulphate or ferrous ammonium sulphate is added gradually to fused ammonium sulphate, products are obtained which differ in composition with the time of heating and the temperature. The excess of ammonium sulphate is separated from the crystalline products by treatment with alcohol.

$Fe_2(SO_4)_3,FeSO_4,4Am_2SO_4 + 3H_2O$ forms colourless, prismatic needles; sp. gr. at $-10° = 2·02$. It dissolves slowly in cold water, and is converted into a basic sulphate by boiling water. It is formed when the quantity of sulphuric acid present is insufficient to convert the whole of the ammonia into ammonium hydrogen sulphate.

$Fe_2(SO_4)_3,3Am_2SO_4$ is obtained by heating the preceding compound in presence of the ammonium salt. It forms white, prismatic needles; sp. gr. = 2·31 at 14°.

$Fe_2(SO_4)_3,Am_2SO_4$ crystallises in hexagons; sp. gr. at 14° = 2·45. It is obtained when the heating is prolonged.

$Fe_2(SO_4)_3$ is obtained in yellow, hexagonal lamellæ (sp. gr. 3·05 at 14°) when any of the preceding compounds is subjected to prolonged heating in presence of ammonium sulphate.

Ferric oxide is obtained by heating the two preceding salts, and forms hexagonal lamellæ of sp. gr. 4·95 at 14°. C. H. B.

Action of Hydrogen Peroxide on the Oxides of Molybdenum, Tungsten, and Vanadium. By J. B. Cammerer (*Chem. Zeit.*, **15**, 957—959).—The author prepared a pure molybdic acid from its ammonium salt by repeated ignition and treatment with nitric acid. On boiling this product with a solution of hydrogen peroxide, it gradually dissolves with evolution of oxygen. The resulting liquid is clear yellow, but yields on spontaneous evaporation a thickish, orange-red mass, which may be further dried, and then yields a yellow powder. It is difficultly soluble in cold, but readily so in hot water, and does not again precipitate on cooling. The solution has a strongly acid reaction, combines, however, with acids to form nearly colourless products, and decomposes alkaline carbonates with the formation of colourless salts. Analysis showed it to be not a mixture, but a chemical compound of molybdic acid with hydrogen peroxide of approximately the formula $2MoO_3,H_2O,H_2O_2$. The hydrogen peroxide cannot be expelled by prolonged heating at 100°.

Action on Tungstic Acid.—The acid was prepared in a similar manner to the molybdic acid, and boiled with the solution of hydrogen peroxide, in which it dissolved with evolution of oxygen. The solution behaves like that of the molybdate compound, and cannot be made to crystallise even after the addition of alcohol and ether. On analysis, it proved to be a compound of tungstic acid with hydrogen peroxide, and had the formula WO_3,H_2O,H_2O_2.

Action on Vanadic Acid.—The acid was prepared in the same manner as the two previous compounds, and then boiled with the peroxide. The liquid is first of a dirty-green colour, but evolves oxygen, and then changes to a reddish-brown. On spontaneous evaporation, blackish-brown crusts are obtained, which occasionally show a metallic lustre. The powder is brown and amorphous. Attempts at crystallisation failed. It is but partly soluble in cold water, and on warming, it is gradually decomposed. In dilute acids, it is freely soluble, and loses in colour, especially on warming. Its solution, which is intensely acid to blue litmus-paper, gives with an alkaline carbonate a brown precipitate, which dissolves on warming with evolution of carbonic anhydride.

Analysis, however, showed such a wide variation in the amount of hydrogen peroxide, and the compound is so readily decomposed, that it may be considered more like a mixture than a true chemical combination. L. de K.

Reduction of Potassium Platinum Thiostannate: Potassium Thioplatinosate. By R. Schneider (*J. pr. Chem.* [2], **45**, 401—411).—Potassium platinum thiostannate, $K_2S,3PtS,SnS_2$ (*Annalen*, **138**, 612), is best prepared by melting 1 part of platinum sponge with 2 parts of stannic sulphide (mosaic gold), 6—8 parts of dry potassium carbonate, and 6—8 parts of sulphur. When this salt is heated to dark redness in a current of hydrogen, it loses sulphur as hydrogen sulphide and a mixture of *potassium thioplatinosate*, K_2PtS_2 with platinum and tin is left. When the residue is treated with water in absence of air, the solution contains $K_2PtS_2 + 4KOH$, and there are left undissolved a double salt, $K_2PtS_2,2H_2PtS_2$, platinum,

and tin. When the solution is exposed to the air, the potassium thioplatinosate is partially oxidised according to the equation $3K_2PtS_2 + 3O = K_2PtO_3 + 2K_2PtS_3$, and when this oxidised solution is treated with hydrochloric acid, platinum bisulphide is precipitated. When the insoluble matter left by the treatment of the residue from the heating in hydrogen with water is attacked by dilute hydrochloric acid in absence of air, the K_2PtS_2 becomes H_2PtS_2; in presence of air, this latter is oxidised to H_2O and PtS_2.

Attempts to isolate potassium thioplatinosate failed.

A. G. B.

Mineralogical Chemistry.

Allotropism of Amorphous Carbon. By W. Luzi (*Ber.*, **25**, 1378—1385).—A graphitite is found in the chalk at Wunsiedel, in the Fichtelgebirge, which has been examined by Fuchs, who came to the conclusion that it is amorphous (*J. pr. Chem.*, **7**, 353), and by Sandberger, who also concluded that it is amorphous and identical with the graphitoïd or schungite of Sauer and Inostranzeff. The author considers it to belong to the class of graphitites. He has received from Stugard, in Finnland, a graphitite which is exactly like that of Wunsiedel. It marks paper like graphite, has no plane of cleavage, and has a conchoïdal fracture; sp. gr. = 2·255—2·26 at 17·5°. It gives 0·67 per cent. of pale-yellow ash on combustion in oxygen, and is quite amorphous.

The mineral from Wunsiedel has a sp. gr. = 2·007, is similar to the above in other properties, and is free from hydrogen and nitrogen. When oxidised with potassium chlorate and concentrated, red, fuming nitric acid, it does not behave like ordinary amorphous carbon, but like graphite and graphitite, and yields a graphitite oxide similar to that obtained from magnetic graphitite. After five treatments with the oxidising mixture, the product has an orange-brown colour. It decomposes on heating with hissing and glowing, and leaves a black, powdery, heavy residue. It is insoluble in water and nitric acid, under the microscope is seen to consist of minute leaflets, is doubly refractive, and gave on analysis 51·99 per cent. C, 1·93 per cent. H, 46·08 per cent. O.

From these results, the author concludes that the mineral contains amorphous carbon, which is not identical with the ordinary amorphous modification of this element. E. C. R.

Fractional Analysis of Silicates. By F. W. Clarke (*Chem. News*, **65**, 188—189, 199—200).—The author realises the desirability of furnishing experimental data upon which to base the structural composition of silicates, and, with this object in view, gives the results of some experiments on minerals mainly belonging to the mica and chlorite group, and a few other magnesian silicates such as talc, serpentine, and olivine, the last being the only anhydrous

mineral used. First of all, by ascertaining the loss of weight at 100°, 250°, 300°, and at a full red heat, and when there was fear of oxidation also taking a total water directly, the vermiculite micas, kerrite, jefferisite, and protovermiculite are found to correspond with an ordinary mica, *plus* 3 mols. H_2O, and with hydrogen equivalently replacing the alkali metals of the original mineral; the water is expelled, 2 mols. at 100°, the third at 250°. In the true micas and chlorites the water is not expelled in fractions, but is stable up to or near redness, and is regarded as constitutional. Such results can be turned to account, in many instances, for ascertaining the character and distribution of the hydroxyl, and for finding whether it is in combination with silica, alumina, or magnesia, &c. For instance, in the above minerals all except talc are decomposable by aqueous hydrochloric acid, but by dry hydrogen chloride they are differently affected; this, the following experiments tend to show, is due to the character of the hydroxyl. Each silicate was heated to constant weight in a current of dry hydrogen chloride, at about 400°, a temperature at which the water of constitution is retained. Olivine, which does not contain hydroxyl, was practically unattacked; talc, the true micas, and the vermiculites were not acted on, or only slightly; serpentine and the chlorites, however, were strongly affected, with the production of magnesium chloride, in which the magnesia was estimated, and the numbers obtained lead to the assumption that the group Mg·OH is present in those minerals, which are vigorously attacked by dry hydrogen chloride. It is therefore presumed that talc, which is not attacked either by wet or dry hydrochloric acid, does not contain this group; therefore, of the two suggested formulæ for that mineral, $Mg_3H_2(SiO_3)_4$ and $Mg(Si_2O_5{\cdot}Mg{\cdot}OH)_2$, the former, the acid metasilicate formula, is preferable. This is also supported by the fact that when talc is sharply and quickly ignited one-fourth of its total silica is set free, as represented by the equation $Mg_3H_2Si_4O_{12} = 3MgSiO_3 + SiO_2 + H_2O$; this could not well be explained from the pyrosilicate point of view. Moreover, the acid character of the hydroxyl agrees well with the stability towards acids.

Another method of obtaining further information as regards the composition of these silicates is based on the fact that even if they are readily decomposed by hydrochloric acid, yet by ignition they are transformed into soluble and insoluble portions, for instance, three chlorites of similar type and xanthophyllite (waluewite from Siberia), all of which had been analysed, were strongly ignited over a blast, in a covered platinum crucible, for several hours, digested with strong hydrochloric acid, evaporated to dryness, heated with weak acid, filtered, the silica removed by boiling with solution of sodium carbonate, and the insoluble residue washed, weighed, and separately analysed. In each of the four cases it proved to have the composition of spinel, and in quantity bore a definite relation to the formulæ of the original minerals, which were:—

Ripidolite (West Chester, Pa.), $Al_{38}Mg_8H_{140}(SiO_4)_{50}O_{113}$.
Clinochlore (Slatoust., Urals), $Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$.
Leuchtenbergite (Slatoust., Urals), $Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{124}$.
Waluewite (Slatoust., Urals), $Al_{80}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$.

In each case there is an excess of oxygen over the silica, and the amount of spinel formed by ignition is almost quantitatively proportional to that excess. Such decompositions give strong evidence of the relative constitution of the minerals. The three examples of chlorites all reduce to the general formula $Mg_2(SiO_4)_2R'_4$, in which R′ is partly hydrogen, partly Mg·OH and partly ·AlH_2O_2; the juxtaposition of the two latter groups would explain the formation of spinel on ignition, whilst the soluble portions of the decomposed material are apparently mixtures of olivine and magnesian garnet, minerals which are common sources of chlorites in nature. Tschermak suggested that these particular chlorites were mixtures of amesite and serpentine; as, however, the latter mineral when ignited yields insoluble enstatite, that view, in face of the present results, is untenable. Waluewite, the most basic known member of the clintonite group, appears to be a mixture of isomorphous molecules, among which the compound $(AlO_2Mg)_4SiO_4$ is predominant; such a compound might easily split up into olivine and spinel, $Mg_2SiO_4 + 2MgAl_2O_4$, and the quantity of spinel actually formed, when waluewite is decomposed by heat, is almost exactly the amount required by this theory. The association of spinel and members of the olivine group with clintonite micas in nature is very suggestive in this connection.

D. A. L.

Native Iron from Cañon Diablo. By Mallard and by Daubrée (*Compt. rend.*, **114**, 812—814).—A specimen of native iron, collected by Foote in 1891 near the Cañon Diablo, in Arizona, was found by Koenig to contain cavities filled with black matter, and containing diamonds of 0·5 mm. diameter (this vol., p. 284). In other samples collected by Eckley Coxe, Mallard finds cavities filled with black matter and containing rounded grains of carbonado, 0·5 to 1·0 mm. in diameter. This native iron seems to be of meteoric origin, but Foote observed, about 3 kilom. to the north-west of the locality where the larger fragments are found, an abrupt elevation which seems to be an extinct volcano. It is not improbable, therefore, that the native iron is of terrestrial and volcanic origin.

Daubrée points out that the native iron of Greenland has been shown to be of terrestrial origin, and to be connected with basaltic eruptions. He considers that the determination of the origin of the native iron of the Cañon Diablo would probably throw much light on the general question of the formation of diamonds. C. H. B.

Organic Chemistry.

Boiling Point Curves for the Normal Paraffins. By G. Hinrichs (*Compt. rend.*, **114**, 1015—1018).—In a former paper (*Compt. rend.*, **112**, 998), the author has shown that the boiling point depends on the atomic weight and on the pressure separately. In the present paper, he shows that in an homologous series, that of the normal paraffins, the boiling points are determined by the same

function when the pressure or molecular weight is altered. This is first demonstrated by construction of the isobaric lines for 15, 30, 50, 100, and 760 mm. for the paraffins containing from 11 to 19 carbon atoms. The form of the curves is the same, and they can all be expressed generally by the equation $t = \eta + k_1(\log a - \xi)$, where a is the molecular weight. A like similarity is noticed in the isosomatic curves, where the boiling point is given for each separate paraffin as a function of the pressure. H. C.

Mechanical Determination of the Boiling Points of Compounds with Simple Terminal Substitution. By G. Hinrichs (*Compt. rend.*, **114**, 1113—1115).—The substitution of a simple atom such as that of chlorine, bromine, or iodine for one of the terminal hydrogen atoms in an organic compound will have the effect of increasing the mass and the moment of inertia of the molecule. The boiling point is, as the author has shown, a function of the moment of inertia, and it should be possible from the increase in the latter to calculate the increase of the former. The author shows that this is possible, making use of relationships which he has established in former papers, and that the rise in the boiling point is directly proportional to the increase in the mass, and inversely proportional to the number of carbon atoms in the hydrocarbon molecule. That this result is in keeping with experiment is shown by reference to the bromides and iodides of the C_4, C_5, and C_6 paraffins. H. C.

Establishment of Fundamental Formulæ for the Calculation of Moments of Inertia. By G. Hinrichs (*Compt. rend.*, **114**, 1064—1066).—The author obtains general expressions for the moment of inertia of molecules of the C_nH_{2n+2} hydrocarbons round their natural axes of rotation in terms of the number of carbon atoms contained in the molecule. H. C.

Composition of Ant Oil. By C. Schall (*Ber.*, **25**, 1489—1490). The author has succeeded in separating a hydrocarbon from a specimen of ant oil; it boils at 192—194° under a pressure of 720 mm., and appears to be identical with normal undecane. J. B. T.

Acetylated Lactose and the Optically Different Modifications of Lactose. By M. Schmoeger (*Ber.*, **25**, 1452—1455).—Herzfeld (Abstr., 1880, 619) prepared an octacetyllactose by Liebermann's method, and stated that it melts at 87°; the author finds that, if slowly crystallised from a mixture of alcohol and chloroform, it melts at 95—100°. When separated from its boiling alcoholic solution, it melts at 85°. Its specific rotatory power is $[\alpha]_D = -3{\cdot}5°$.

An acetyllactose was prepared by Schützenberger (*Annalen*, **84**, 74) by the action of acetic anhydride on lactose dissolved in acetic acid. The product of the action is a horny mass melting at about 80°, and containing about 40 per cent. of acetyl. By fractional crystallisation from water, the author succeeded in separating a small quantity (4 per cent.) of the crystalline octacetyllactose from it, the remainder was an amorphous mass consisting, probably, of acetylated decomposition products. On attempting to prepare a hydrazone and

osazone from this, only acetylphenylhydrazine was obtained. No crystalline product was formed with hydroxylamine.

The author has previously pointed out the existence of two optically different modifications of ordinary lactose (Abstr., 1882, 157). The one exhibiting semi-rotation is obtained by rapidly evaporating a solution of 2·6 grams of lactose on a water-bath. The modification showing slight bi-rotation is prepared by evaporating not more than 7 c.c. of a 10 per cent. sugar solution to dryness. The two modifications are crystalline, and contain no water of crystallisation; they eventually change into the variety showing constant rotatory power. Cryoscopic determinations and observations of their refractive indices and dispersions in aqueous solution afford no explanation of their existence. W. J. P.

Allyltrimethylammonium Chloride and Iodide. By E. Schmidt and J. Weiss (*Annalen*, **268**, 143—151; compare this vol., p. 905, and Bode, this vol., p. 806).—*Allyltrimethylammonium chloride*, $NMe_3Cl{\cdot}C_3H_5$, is formed when allyl chloride is treated with methylamine in alcoholic solution; it is a colourless, very hygroscopic, crystalline compound, which seems not to be reduced on treatment with tin and hydrochloric acid. The *platinochloride*, $(NMe_3Cl{\cdot}C_3H_5)_2,PtCl_4$, separates from dilute hydrochloric acid in well-defined octahedra, and melts at 215°; when its aqueous solution is boiled for a long time and then allowed to cool, a lemon-yellow salt of the composition

$$NMe_3Cl{\cdot}C_3H_5,PtCl_2,$$

is deposited. The *aurochloride*, $NMe_3Cl{\cdot}C_3H_5,AuCl_3$, crystallises in golden plates, and melts at 210°.

Propyltrimethylammonium iodide, NMe_3IPr, prepared from normal propyl iodide in like manner, is a colourless, crystalline compound. When treated with silver chloride, it yields a chloride from which an *aurochloride* of the composition $NMe_3ClPr,AuCl_3$ is obtained; this crystallises in long, golden needles, melts at 215°, and is quite different in properties from the aurochloride which is obtained from the allyl base after the latter has been treated with tin and hydrochloric acid.

When allyltrimethylammonium chloride is treated with bromine in alcoholic solution, it is converted into a *perbromide* of the composition $NMe_3Br{\cdot}C_3H_5Br + Br_2$; this compound forms well-defined, reddish-yellow crystals, and is converted into dibromopropyltrimethylammonium bromide (m. p. 173°) by warm alcohol.

Allyltrimethylammonium iodide, $NMe_3I{\cdot}C_3H_5$, prepared from allyl iodide and trimethylamine, separates from boiling alcohol in well-defined, colourless needles, and melts at 104°.

Experiments on frogs and rabbits showed that the physiological action of allyltrimethylammonium salts is quite different from that of neurine, the former being far less poisonous than the latter.

F. S. K.

Note by Abstractor.—The melting points of some of the compounds described above are not given by the author, but are taken from Partheil's paper (compare following abstract) to avoid repetition.

Derivatives of Allyltrimethylammonium Hydroxide. By E. Schmidt and A. Partheil (*Annalen*, **268**, 152—197; compare Abstr., 1890, 356, and Schmidt, this vol., p. 905).—These experiments were instituted in order to compare the chemical behaviour of allyltrimethylammonium hydroxide with that of the corresponding vinyl compound, and also with the object of preparing and studying the physiological action of homologues of isomuscarine and of acetenyltrimethylammonium hydroxide; practically the whole of the subject matter of the present paper has already been published (Abstr., 1890, 356).

Tetramethylammonium bromide, prepared as already described (compare Schmidt, this vol., p. 805), crystallises from glacial acetic acid in prisms, and from water and alcohol in octahedra; it is insoluble in ether and acetone, and only very sparingly soluble in cold alcohol.

When *dibromopropyltrimethylammoninm bromide*, $NMe_3Br\cdot C_3H_5Br_2$, (m. p. 173°) is decomposed with silver chloride, and the hydrochloric acid solution of the product mixed with auric chloride, an *aurochloride* of the composition $NMe_3Cl\cdot C_3H_5Br_2,AuCl_3$ is deposited in lemon-yellow needles, melting at 148°; by directly precipitating a solution of the bromide with auric chloride, the same aurochloride is obtained, mixed, however, with some other bromo-derivative.

When γ-iodopropyltrimethylammonium iodide (*loc. cit.*) is treated with moist silver oxide at the ordinary temperature, it is converted into the corresponding hydroxide, the *platinochloride*,

$$(NMe_3Cl\cdot C_3H_6I)_2,PtCl_4,$$

of which crystallises from hot, dilute hydrochloric acid in brownish-red needles, melting at 237°; if, however, the treatment is carried out at 100°, or alcoholic potash is employed instead of silver oxide, allyltrimethylammonium hydroxide is produced with liberation of hydriodic acid; when boiled with silver nitrate, the iodide is converted into γ-hydroxypropyltrimethylammonium hydroxide (γ-homocholine), identical with the compound described by Weiss (*Zeitschr. f. Naturw.*, **60**, 275).

When trimethylenechlorhydrin is heated at 100° for six hours with an alcoholic solution of trimethylamine, there is formed a salt which seems not to be identical with homocholine hydrochloride.

F. S. K.

Picric Acid as a Reagent for Guanidine. By O. Prelinger (*Monatsh.*, **13**, 97—100; compare Emich, Abstr., 1891, 1180).—*α-Triphenylguanidine picrate*, $CH_2Ph_3N_3,C_6H_2(NO_2)_3\cdot OH$, is readily formed on shaking together equivalent quantities of the base and acid dissolved in hot alcohol. It is of a deep-yellow colour; melts at 176—178°; dissolves in 12,200 parts of water at 15°; is only sparingly soluble in ether, benzene, and carbon bisulphide, but may be readily recrystallised from chloroform or acetone.

Phenylguanidine picrate is obtained in the form of deep-yellow, slender, microscopic needles on adding picric acid to a solution of phenylguanidine. It melts partly at 208°, completely at 214°, is nearly insoluble in water, but dissolves readily in acetone.

The relative insolubility in water of the compounds described above, leads the author to suggest that picric acid may be employed with advantage as a reagent for the detection of guanidine and its derivatives. G. T. M.

Action of Nitric Acid on the Amidines. By A. P. N. Franchimont (*Rec. Trav. Chim.*, **10**, 231—235).—Guanidine nitrate dissolves in an excess of nitric acid with development of heat, but without the production of any gas. The product, recrystallised from boiling water, forms slender needles which decompose at 222°.

Nitroguanidine, suspended in absolute alcohol and subjected to the action of a current of dry ammonia, dissolves after some time. From the solution, by diluting with water and neutralising, a substance which appears to be nitroguanidine is re-obtained. After some time, the solution yields a well-crystallised residue which is soluble in water, but only slightly in alcohol. Nitroguanidine dissolves easily in aqueous ammonia; the solution gives off nitrogen monoxide at the ordinary temperature. The reaction may be written $C(NH_2)_2{:}N{\cdot}NO_2 + H_2O = CO(NH_2)_2 + NH_2{\cdot}NO_2$; the carbamide decomposes in presence of a base into ammonia and carbonic anhydride; the nitramine immediately forms water and nitrogen monoxide.

Attempts to prepare the sodium derivative of this, the simplest, nitramine by the action of sodium alkyl oxides on nitroguanidine failed. Propionamidine appears not to form a nitro-derivative even when evaporated with 10 times its weight of nitric acid. Its nitrate crystallises in colourless, deliquescent prisms melting at 132°. W. T.

Action of Sulphuric Acid on Methylethylacraldehyde. By E. Ludwig (*Ber.*, **25**, 1409—1410).—Methylethylacraldehyde is entirely resinified when suspended in water and treated with concentrated sulphuric acid. If, however, it is added to an ice-cold mixture of alcohol and sulphuric acid, only a small quantity of resin is formed, together with a *hexenylsulphuric acid* of the composition $CH_2Me{\cdot}CH_2{\cdot}CMe[CH(OSO_3H)_2]{\cdot}OSO_3H$. Methylethylacraldehyde (5 grams) is added drop by drop to an ice-cold mixture of alcohol (20 grams) and sulphuric acid (30 grams). The solution is separated from the resin, calcium carbonate added, and the mixture filtered. On concentrating the filtrate, the easily soluble *calcium* salt of the acid is obtained, and crystallises when placed in a vacuum over sulphuric acid. The *barium* salt, obtained by adding barium hydrate to the crude product, is very easily soluble, and is crystalline. When the acid is heated with potassium hydroxide at 100°, sulphuric acid is not eliminated. When distilled with potassium hydroxide, slight carbonisation takes place, an alcoholic liquid distils over, and potassium sulphate remains.

The author is engaged in the further investigation of these reactions. E. C. R.

Acetaldoxime. By A. P. N. Franchimont (*Rec. Trav. Chim.*, **10**, 236—237).—Acetaldoxime has been described by V. Meyer and by Petraczek (Abstr., 1883, 569) as a liquid boiling at 114—115°. The

author finds it to be a solid substance, distilling constantly at 114·5°, melting at 47°, and solidifying, even in a capillary tube, immediately on taking from the bath. It is an inodorous substance, crystallising in acicular crystals sometimes a decimetre in length. It dissolves easily in ether, chloroform, acetone, and benzene, less easily in petroleum ether and carbon bisulphide. There seems no reason to believe that this substance is an isomeride of the ordinary acetaldoxime. The author suggests that a trace of impurity prevents the crystallisation of the ordinary substance. (Compare Dunstan and Dymond, Trans., 1892, 470, and Proc., 1892, 135.) W. T.

Preparation of Symmetrical Dichloracetone. By A. Erlenbach (*Annalen*, **269**, 46—48).—In preparing symmetrical dichloracetone by the method described by Grimaux and Adam (*Bull. Soc. Chim.*, **36**, 19), the yield is increased from 15 to 57 per cent. of the oxidised dichlorohydrin by proceeding as follows:—Dichlorhydrin (100 grams) and very finely divided potassium dichromate (80 grams) are placed in a litre flask, and a mixture of concentrated sulphuric acid (120 grams) and water (150 grams) is added in small quantities at a time in the course of a day to the ice-cold solution, which is frequently and vigorously shaken; after keeping over night, the oil is extracted with ether, and the dichloracetone separated from unchanged dichlorhydrin with the aid of sodium hydrogen sulphite. F. S. K.

Diamidoacetone. By L. Rügheimer and E. Mischel (*Ber.*, **25**, 1562—1568).—Rügheimer (Abstr., 1889, 249 and 1210) has obtained diamidoacetone from several compounds, and has described the sulphate and the platinochloride. The base cannot be isolated, and its aqueous solutions decompose on remaining; the *hydrochloride* $CO(CH_2{\cdot}NH_2,HCl)_2 + 1\frac{1}{2}H_2O$, which forms lustrous crystals soon becoming dull, the *nitrate*, the picrate, and the aurochloride have all been obtained in the crystalline form.

Benzenyldiamidoacetone, $CO<\begin{matrix}CH_2{\cdot}NH\\CH_2{-}N\end{matrix}>CPh$, is produced when an aqueous solution of diamidoacetone sulphate is rendered slightly alkaline and benzoic chloride (1 mol.) gradually added with vigorous shaking; it crystallises from alcohol in colourless leaflets, and melts at 190—191°. It is a neutral compound, and reduces ammoniacal silver and Fehling's solutions. When suspended in absolute alcohol, and treated with hydrazine hydrate, the *compound* $N_2(C<\begin{matrix}CH_2{\cdot}NH\\CH_2{-}N\end{matrix}>CPh)_2 + 2H_2O$ is obtained; the phenylhydrazone,

$$N_2HPh{:}C<\begin{matrix}CH_2{\cdot}NH\\CH{-}N\end{matrix}>CPh,$$

crystallises from alcohol in needles which are sensitive towards light and heat, and melt at 173—175°. *Phenylethenyldiamidoacetone*, $CO<\begin{matrix}CH_2{\cdot}NH\\CH_2{-}N\end{matrix}>C{\cdot}CH_2Ph$, prepared from diamidoacetone sulphate and phenylacetic chloride, forms colourless, lustrous leaflets, and melts at 189·5—190·5°, being fairly soluble in hot water, but insoluble in ether;

it reduces ammoniacal silver solution on heating, and Fehling's solution at the ordinary temperature.

When a concentrated solution of diamidoacetone sulphate (1 mol.) is mixed with potassium carbimide (2 mols.) crystals separate, but redissolve after a time, and at the end of some days an amorphous compound separates which is insoluble in alcohol, but readily soluble in water, melts at about 224°, and is perhaps the *biuret*,

$$CO<\begin{matrix}CH_2\cdot NH\cdot CO\\CH_2\cdot NH\cdot CO\end{matrix}>NH.$$

Ethyl chlorocarbonate reacts with diamidoacetone forming a white crystalline compound, probably $CO<\begin{matrix}CH_2\cdot NH\\CH_2\cdot NH\end{matrix}>CO$. A. R. L.

Cuprammonium Acetobromide. By P. W. Richards (*Ber.*, **25**, 1492).—*Cuprammonium acetobromide*, $CuBr,Ac,2NH_3$, is prepared by mixing together cupric bromide (5 grams), alcohol (10 c.c.), and saturated alcoholic ammonia (10 c.c.); the precipitate which forms is immediately dissolved in a mixture of acetic acid (16 c.c.) and alcohol (70 c.c.); on allowing the solution to evaporate spontaneously in the air, or on cooling it to −5°, lustrous, prismatic crystals separate which probably belong to the monosymmetric system; the compound is almost insoluble in alcohol, but decomposes in presence of water. J. B. T.

Ethyl Acetoacetate. By P. C. Freer (*J. pr. Chem.* [2], **45**, 414—416).—Brühl (this vol., p. 583) admits that the behaviour of ethyl acetoacetate with phenylhydrazine (Nef, this vol., p. 142) is one of the instances in which this ethyl salt behaves as a hydroxycrotonic derivative. Inasmuch as phenylhydrazine is a base, its behaviour to ethyl acetoacetate should resemble that of sodium; the author has experimented with phenylhydrazine hydrochloride, expecting to obtain some different result.

Phenylhydrazine hydrochloride was added to a solution of ethyl acetoacetate in absolute alcohol, together with some chalk to keep the liquid neutral; carbonic anhydride was evolved, and the reaction was over in the course of 6—8 hours. When the product was poured into water, a yellow oil separated; this was dissolved in ether, the ethereal solution was washed successively with sodium hydroxide, dilute hydrochloric acid, and water, dried, and distilled. The residual yellow oil, $C_{10}H_{10}N_2O$, boiled at 220° (30 mm.), and became brown in air; its empirical formula is identical with that of 1-phenyl-3-methyl-5-pyrazolone; the hydrochloride, $C_{10}H_{11}N_2OCl$, was prepared.

By acidifying the alkaline washings of the above ether extract with hydrochloric acid, a difficultly crystallisable acid was isolated, but not further investigated; when this was filtered off, and sodium carbonate added to the filtrate, 1-phenyl-3-methyl-5-pyrazolone (m. p. 127°) was precipitated. A. G. B.

Action of Sodium on Ethyl Chloracetate. By A. Erlenbach (*Annalen*, **269**, 14—48).—*Ethyl ethoxychloracetoacetate*,

$$OEt\cdot CH_2\cdot CO\cdot CHCl\cdot COOEt,$$

or $CH_2Cl{\cdot}CO{\cdot}CH(OEt){\cdot}COOEt$, is formed, together with at least two other compounds, when ethyl chloracetate (100 grams) is added in the course of $1\frac{1}{2}$ days to ice-cold ether (200 grams) containing shavings of sodium (27 grams) in suspension; two days after the commencement of the experiment, the greater part of the sodium has disappeared, the evolution of hydrogen is almost at an end, and from the dark red ethereal solution a light yellow powder has been deposited. The unchanged sodium is then separated by filtration through a coarse metallic sieve, the solution containing the solid in suspension is mixed with water and dilute hydrochloric acid, the ethereal layer separated, dried, evaporated, and the ethyl ethoxychloracetoacetate isolated from the oily mixture by fractional distillation, under a pressure of 40—60 mm., during which process hydrogen chloride is evolved; the weight of the pure compound is, on the average, half that of the ethyl chloracetate employed. It is a yellowish liquid, and boils at 157° under a pressure of 45 mm., and at 162° under a pressure of 55 mm., but it cannot be distilled under the ordinary atmospheric pressure; it is only sparingly soluble in water, but it dissolves in dilute soda, and in sodium carbonate, with partial decomposition, yielding a dark brown solution. When boiled with dilute hydrochloric acid, it is decomposed into alcohol, carbonic anhydride, and symmetrical dichloracetone. The *sodium* derivative, $C_8H_{12}ClO_4Na$, is a colourless powder, and is decomposed by water. The *copper* derivative is a green, crystalline compound.

Ethyl ethoxyacetoacetate, $C_8H_{14}O_4$, can be obtained by treating the chloro-derivative just described with zinc dust and acetic acid in the cold; the product is purified by means of its copper derivative. It is a colourless liquid, boils at 105° under a pressure of 14 mm. with very slight decomposition, and just above 200° under the ordinary atmospheric pressure with considerable decomposition; it is moderately easily soluble in water, more readily in dilute hydrochloric acid. The *sodium* derivative is a colourless, gum-like substance. The *copper* derivative $(C_8H_{13}O_4)_2Cu$, prepared by shaking the ethereal salt with a concentrated solution of copper acetate, crystallises from alcohol in long, green needles, melts at 143°, and is insoluble in water, but readily soluble in ether, benzene, chloroform, and carbon bisulphide; when an alcoholic solution of a mixture of the copper derivatives of ethyl ethoxyacetoacetate and ethyl ethoxychloracetoacetate is heated for some time at 80°, a yellow basic substance, consisting principally of the decomposition products of the copper derivative of the chloro-compound, is deposited. The *aluminium* derivative crystallises from cold dilute alcohol in small, colourless needles, and dissolves freely in ether, benzene, chloroform, and light petroleum. When ethyl ethoxyacetoacetate is warmed for a short time with dilute hydrochloric acid, it is decomposed into carbonic anhydride, alcohol, and acetol ethyl ether, $COMe{\cdot}CH_2{\cdot}OEt$, identical with the compound described by Henry (*Compt. rend.*, **93**, 422).

Acetol ethyl ether is a colourless, mobile oil of sp. gr. 0·9204 at 21·7°, boils at 128°, and is miscible with alcohol, ether, and water in all proportions; it reduces solutions of copper acetate and ammoniacal solutions of silver, and when treated with potassium dichromate and

dilute sulphuric acid it is oxidised to acetic acid, carbonic acid and formic acid being also produced in small quantities. It combines very readily with sodium hydrogen sulphite, forming a very readily soluble crystalline compound, and on reduction with sodium amalgam in acid solution, it yields approximately equal quantities of acetone and ethyl alcohol, together with traces of isopropyl alcohol. The *hydrazone*, $N_2HPh{:}CMe{\cdot}CH_2{\cdot}OEt$, is a yellowish oil, boils at 165° under a pressure of 16 mm., and at 267° with decomposition under the ordinary atmospheric pressure; it turns brown on exposure to the air, and dissolves freely in ether and alcohol, but is insoluble in water.

Ethoxymethylindole, $C_{11}H_{13}NO$, is formed when the hydrazone just described is heated with sodium acetate, a little sodium chloride, and a few drops of acetic acid in dilute alcoholic solution; it separates from alcohol in large, colourless, rhombic crystals, $a : b : c = 0{\cdot}5635 : 1 : 0{\cdot}7445$, melts at 143·5°, and is readily soluble in ether, alcohol, benzene, and chloroform, but more sparingly in light petroleum and cold water; it is not acted on by dilute soda, and is only very slowly decomposed by dilute hydrochloric acid.

Ethyl diethoxyacetoacetate, $OEt{\cdot}CH_2{\cdot}CO{\cdot}CH(OEt){\cdot}COOEt$, can be obtained by gradually adding ethyl ethoxychloracetoacetate to a cold alcoholic solution of sodium ethoxide, and then boiling the mixture for three hours. It boils at 131—132° under a pressure of 11 mm., and is identical with the compound prepared by Conrad from ethyl ethylglycollate (*Ber.*, **11**, 58); when boiled with dilute potash, it is converted into diethoxyacetone (compare Grimaux and Lefèvre, Abstr., 1889, 235), the *sodium* derivative of which is a yellow, hygroscopic substance of the composition $C_7H_{13}O_3Na$.

A compound of the composition $C_{12}H_{14}O_7$, which the author names *ethyl ketacetate*, is deposited in yellow needles when ethyl ethoxychloracetoacetate is mixed with a solution of sodium acetate, and the mixture kept at the ordinary temperature for many days, with frequent shaking. It melts at 140·5°, and is readily soluble in warm alcohol, benzene, chloroform, and carbon bisulphide, but only sparingly in ether, very sparingly in light petroleum, and insoluble in cold water; when a trace of the substance is warmed with water, the latter is coloured an intense bluish-violet, the colour changing to yellow on prolonged boiling. It dissolves freely in ammonia and in soda, and is reprecipitated unchanged on immediately adding dilute hydrochloric acid; the soda solution quickly turns reddish-brown, and after keeping for some time, only a small quantity of a resinous substance is precipitated on the addition of dilute hydrochloric acid; it reduces ammonical silver solutions in the cold. The molecular weight of the compound was determined in glacial acetic acid solution with results which agreed well with those required by a compound of the molecular formula given above. The *sodium* derivative, $C_{12}H_{12}O_7Na_2$, is an almost colourless powder, stable in the air, and soluble in alcohol, yielding a dark green solution. The *barium* derivative, $C_{12}H_{12}O_7Ba + H_2O$. and the *calcium* derivative $C_{12}H_{12}O_7Ca$, are amorphous. The *cuprous* derivative, $C_{12}H_{12}O_7Cu_2$, crystallises in slender, yellow needles. The instability of these metallic derivatives, and the fact that they are decomposed by carbonic anhydride with

regeneration of ethyl ketacetate, renders it highly improbable that the last-named compound is a true carboxylic acid; a number of experiments were made with the object of determining the constitution of the compound, but without success; the most important results bearing on this question are the following:—When ethyl ketacetate is boiled with concentrated hydriodic acid, the quantity of ethyl iodide liberated, determined by Zeisel's method, corresponds with the theoretical quantity for two ethoxy-groups; when treated with soda at the ordinary temperature, it yields an amorphous compound, which seems to have the composition $C_{10}H_{10}O_7$. The *diacetyl* derivative, $C_{12}H_{12}O_7Ac_2$, is formed when ethyl ketacetate is heated with excess of acetic anhydride for 10 hours at 120°, or, better, warmed with acetic chloride at 70—80° for two hours; it crystallises from moderately dilute alcohol in yellow prisms and in colourless needles, melts at 106—107°, and is readily soluble in warm ether, benzene, alcohol, carbon bisulphide, and acetic acid, but insoluble in cold water; it dissolves freely in dilute soda, yielding a yellow solution, from which ethyl ketacetate is precipitated on adding dilute hydrochloric acid. The *dihydrazone*, $C_{24}H_{26}N_4O_5$, prepared by heating ethyl ketacetate with phenylhydrazine, is a red, amorphous compound, readily soluble in ether, benzene, alcohol, and chloroform, but insoluble in light petroleum and water. The *anilide*, $C_{18}H_{19}NO_6$, crystallises from alcohol in golden needles, melts at 137—138°, and dissolves freely in ether and alcohol, but is insoluble in water. The *bromo*-derivative, $C_{12}H_{13}BrO_7$, is formed when ethyl ketacetate is suspended in carbon bisulphide and treated with one molecular proportion of bromine; it separates from a mixture of chloroform and light petroleum in transparent, well-defined, prismatic, colourless or rose-red crystals, melts at 125—130°, and is readily soluble in chloroform and ether, but only sparingly in cold carbon bisulphide and light petroleum; it is decomposed by alcohol, and it becomes sticky on exposure to the air. When ethyl ketacetate is dissolved in ice-cold concentrated nitric acid, and the solution poured into water, a colourless, crystalline compound is deposited after a short time. This product separates from a mixture of ether and light petroleum in large, colourless, well-defined crystals, which melt at 80—95°, decompose at 102°, and have the composition $C_{12}H_{13}NO_{10} + 2H_2O$; when the crystals are kept over sulphuric acid under reduced pressure, they lose water and then melt at 40—45°; the anhydrous substance is very hygroscopic and crystallises from a mixture of ether and light petroleum in radially-grouped needles. F. S. K.

Lactonic Acids, Lactones, and Unsaturated Acids. By R. Fittig (*Annalen*, **268**, 1—7; compare this vol., p. 812).—The further investigation of the oxidation products of unsaturated acids (compare Fittig and Buri, *Annalen*, **216**, 171, **227**, 31, and Regel, Abstr., 1887, 488) has shown that $\alpha\beta$-unsaturated acids are oxidised to stable dihydroxy-acids, whereas the $\beta\gamma$-acids give unstable dihydroxy-acids, which, on liberation from their salts, are converted into neutral hydroxylactones. These lactones, just like the simple lactones, are either unacted on, or only very slowly decomposed by

water, but are readily converted into salts of the corresponding acids on boiling with strong bases; they are more readily soluble in water than the simple lactones, but separate from moderately concentrated solutions on the addition of potassium carbonate.

$\beta\gamma$- and $\gamma\delta$-unsaturated acids show no difference in behaviour on oxidation; allylacetic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, for example, resembles ethylidenepropionic acid, $CHMe{:}CH{\cdot}CH_2{\cdot}COOH$, not only in its behaviour on oxidation, but also in all other reactions, such as in its conversion into valerolactone and in the decomposition of its dibromide; if, therefore, allylacetic acid really is a $\gamma\delta$-unsaturated compound, it is impossible, at present, to distinguish such an acid from a $\beta\gamma$-compound by means of chemical reactions. Hydrosorbic acid gives, on oxidation, two isomeric hydroxylactones, of which one can be partially converted into the other by boiling its alkaline solution; whether this is due to the presence of two isomerides in the hydrosorbic acid, or whether the two lactones are geometrical isomerides, has yet to be determined.

Phenylisocrotonic acid, which is doubtless a pure $\beta\gamma$-unsaturated compound, also gives two hydroxylactones, which resemble one another very closely in chemical behaviour.

The two crotonic acids give, on oxidation, two different dihydroxy-acids, that obtained from isocrotonic acid being identical with Hanriot's dihydroxybutyric acid.

In all the experiments, which are more fully described in the following abstracts (pp. 958, 959, 960, 986), the oxidation was carried out as follows:—The unsaturated acid (5 grams) is placed in a flask together with 400—500 c.c. of water, the solution rendered strongly alkaline with sodium carbonate or soda, and then a 2 per cent. solution of potassium (or barium) permanganate gradually added to the ice-cold solution; as a rule, molecular proportions of the acid and of potassium permanganate were employed. As bye-products, oxalic acid, succinic acid, and aldehydes are sometimes obtained, and in the case of some of the aromatic compounds benzoic acid is formed. F. S. K.

Oxidation of Crotonic Acid and Isocrotonic Acid. By R. Fittig and E. Kochs (*Annalen*, **268**, 7—22).—*Dihydroxybutyric acid*, $C_4H_8O_4$, is formed, together with aldehyde, acetic acid, and oxalic acid, when solid crotonic acid is oxidised with potassium permanganate in the manner already described (compare preceding abstract); as the acid is isolated only with difficulty, it is better to use barium permanganate ($\frac{1}{2}$ mol.) in place of the potassium salt. It separates from water in long, transparent, prismatic crystals, containing 1 mol. H_2O, which lose their water over sulphuric acid, and then melt at 74—75°; the anhydrous substance deliquesces in moist air. It is very readily soluble in water, alcohol, and acetone, but almost insoluble in hot ether, light petroleum, and chloroform; it is not volatile with steam, and is not changed by boiling, dilute hydrochloric acid. The *calcium* salt, $(C_4H_7O_4)_2Ca$, is a colourless, vitreous compound, very readily soluble in water, but insoluble in alcohol. The *barium* salt, with 2 mols. H_2O, separates from cold water in microscopic, prismatic crystals. The *silver* salt, $C_4H_7O_4Ag$, forms

microscopic, lance-shaped needles, and large, lustrous plates, and is only sparingly soluble in cold, but more readily in hot water, by which it is partially decomposed. This dihydroxybutyric acid is possibly identical with the compound obtained by Kolbe (*J. pr. Chem.*, **25**, 391) from $\alpha\beta$-dibromobutyric acid, and also with that prepared by Melikoff (Abstr., 1886, 1008) from β-methylglycidic acid.

Isodihydroxybutyric acid, $C_4H_8O_4$, obtained by the oxidation of pure isocrotonic acid, is a syrup, readily soluble in acetone, but insoluble in ether. The calcium salt, $(C_4H_7O_4)_2Ca$, and the barium salt, are brittle, vitreous compounds, readily soluble in water. The silver salt, $C_4H_7O_4Ag$, crystallises from pure hot water in small needles, quickly turns yellow on exposure to light, and is partially decomposed by boiling water; it is $3\frac{1}{2}$ times as readily soluble in water at 12—13·5° as the silver salt of the isomeric dihydroxybutyric acid described above. Isodihydroxybutyric acid is, in all probability, identical with the compound described by Hanriot (*Ann. Chim. Phys.* [5], **17**, 104) and by Melikoff (*Ber.*, **15**. 2587).

When either of the dihydroxybutyric acids is heated at 100° for eight days, an amorphous substance of the composition $C_8H_{10}O_5$ is formed, probably an anhydride of complex constitution.

F. S. K.

Oxidation of Ethylcrotonic Acid. By R. Fittig and R. Ruer (*Annalen*, **268**, 22—27).—*Isohexeric acid*, $C_6H_{12}O_4$, isomeric with the hexeric acid described by Fittig and Howe (*Annalen*, **200**, 38), is produced, together with a small quantity of oxalic acid, when ethylcrotonic acid is oxidised with potassium permanganate. It crystallises from a mixture of benzene and light petroleum in small plates, melts at 95—96°, and is readily soluble in water, but more sparingly in ether, chloroform, and benzene, and almost insoluble in light petroleum; it is not changed by boiling dilute hydrochloric acid, and it is not converted into an isomeride by boiling barium hydroxide. The *calcium* salt, $(C_6H_{11}O_4)_2Ca + 3H_2O$, forms small, nodular crystals, loses 2 mols. H_2O at 100°, and a third between 100° and 125°; it is readily soluble in water. The *barium* salt, $(C_6H_{11}O_4)_2Ba$, is an amorphous compound, very readily soluble in water, but only very sparingly in alcohol. The *zinc* salt separates from water in crystals containing 1 mol. H_2O.

F. S. K.

Oxidation of Allylacetic Acid. By R. Fittig and K. Urban (*Annalen*, **268**, 32—38).—*Hydroxyvalerolactone*,

$$\begin{matrix} CO—O \\ | \\ CH_2\cdot CH_2 \end{matrix} > CH_2\cdot CH_2\cdot OH,$$

obtained together with succinic acid, by the oxidation of allylacetic acid with potassium permanganate, is a colourless, moderately mobile liquid, boils at 300—301° with only slight decomposition, and is very readily soluble in water, but only sparingly in ether; it is slowly decomposed by cold, more quickly by boiling water, and it separates from moderately concentrated aqueous solutions on the addition of solid potassium carbonate.

Salts of dihydroxyvaleric acid are formed when the preceding compound is boiled with bases, but the acid cannot be isolated. The *barium* salt, $(C_5H_9O_4)_2Ba$, is a brittle, amorphous compound, but the *calcium* salt, $(C_5H_9O_4)_2Ca$, separates from concentrated aqueous solutions in crystalline crusts, and is very readily soluble in water, but insoluble in alcohol. The *silver* salt, $C_5H_9O_4Ag$, crystallises in colourless, lustrous plates or needles, and is decomposed by hot water. F. S. K.

Oxidation of Hydrosorbic Acid. By R. Fittig and J. Hillert (*Annalen*, **268**, 38—44).—When hydrosorbic acid is oxidised with potassium permanganate, a small quantity of succinic acid is formed, but the principal product is a neutral liquid which, when boiled with barium hydroxide, gives two barium salts, one of which is crystalline and insoluble in alcohol, the other amorphous and readily soluble in alcohol.

Hydroxycaprolactone, $C_6H_{10}O_3$, is obtained when the crystalline barium salt is decomposed with hydrochloric acid, and the solution immediately extracted with ether; on evaporating the ethereal solution at the ordinary temperature, a crystalline compound—doubtless dihydroxycaproic acid—is deposited, but the crystals quickly change into the liquid lactone. This compound dissolves in water in all proportions, yielding a neutral solution, from which it separates again as an oil on saturating with potassium carbonate; it distils under the ordinary atmospheric pressure, with partial decomposition. When boiled with water, it is only partially converted into dihydroxycaproic acid. *Barium dihydroxycaproate*, $(C_6H_{11}O_4)_2Ba$, prepared as already described, separates from hot water, in which it is very readily soluble, in colourless crystals. The *calcium* salt, $(C_6H_{11}O_4)_2Ca$, is much more readily soluble than the barium salt, and forms small, nodular crystals. The *silver* salt, $C_6H_{11}O_4Ag$, crystallises from warm water in lustrous, colourless needles.

Isohydroxycaprolactone, $C_6H_{10}O_3$, prepared from the amorphous barium salt referred to above, is a thick, colourless liquid, miscible with ether, and resembles the isomeride in its other properties. *Barium isodihydroxycaproate* and the corresponding *calcium* salt are amorphous, anhydrous compounds. The *silver* salt is very unstable.

When a solution of dihydroxycaproic acid is boiled with excess of soda for three hours, about one quarter of the acid is converted into the isomeric iso-compound. F. S. K.

Decomposition of Dibromides of Unsaturated Acids by Warm Water and Dilute Alkalis. By R. Fittig (*Annalen*, **268**, 55—60).—The study of the decomposition of a number of dibrom-additive products of $\beta\gamma$- and $\gamma\delta$-unsaturated acids by boiling water, or by cold dilute alkalis, has shown that they all behave in a similar manner, inasmuch as the first decomposition product is invariably a bromolactone of the constitution $CH_2<\begin{matrix}CO\cdot O\\CHBr\end{matrix}>CH\cdot CH_2X$ or $CH_2<\begin{matrix}CO\cdot O\\CH_2\end{matrix}>CH\cdot CHBrX$; if the treatment with boiling water, or

with dilute alkali, is prolonged, the bromolactone is decomposed into a hydroxylactone and an $\alpha\gamma$-ketonic acid, which are not convertible one into the other. Since the dibromide of allylacetic acid behaves just like the other dibromides, it follows that, assuming that this acid really is a $\gamma\delta$-dibromo-derivative, the position of the bromine atom in the bromolactone has no influence whatever on the manner in which the last-named compound undergoes decomposition. Although all the dibromo-acids behave in the manner just stated, there are certain respects in which they differ; in the case of the fatty compounds, the hydroxylactone is invariably the principal product, the ketonic acid being produced in comparatively small quantities; in the case of the aromatic acids, on the other hand, the ketonic acid is the principal product. and a hydroxylactone is not formed at all, when the decomposition is effected with boiling water, and only in one instance, namely, in the case of isocrotonic acid, when dilute alkali is employed.

The hydroxylactones produced in the manner described above are, as a rule, identical with the compounds obtained directly by the oxidation of the unsaturated acids (compare preceding abstracts) Although hydrosorbic acid yields two isomeric compounds on oxidation, only one hydroxylactone is obtained from its dibromide. The dibromide of phenylisocrotonic acid (phenyldibromobutyric acid) yields two bromolactones under certain conditions; the hydroxylactone obtained from the dibromide is, moreover, quite different from that produced by the oxidation of phenylisocrotonic acid. The author prefers not to attempt any explanation of these cases of isomerism.

The formation of the γ-ketonic acids from the bromolactones is easily explained by assuming that unsaturated lactones are first produced by the elimination of hydrogen bromide; these compounds are rather unstable, as has been shown by Wolff (*Annalen*, **229**, 249), and, by the addition of 1 mol. H_2O, they would be converted into γ-ketonic acids. This view was proved to be correct in the case of phenyldibromovaleric acid, since an intermediate product of this nature (phenylangelicalactone) was actually isolated.

The experimental part of this work is described in the following abstracts, and on p. 987. F. S. K.

Decomposition of Dibromovaleric Acid. By R. Fittig and K. Urban (*Annalen*, **268**, 60—67).—*Bromovalerolactone*, $C_5H_7BrO_2$, is easily obtained by dissolving dibromovaleric acid (m. p. 58°) in a slight excess of sodium carbonate, and, after a short time, extracting the precipitated oil with ether. It is a colourless, mobile liquid, and is only sparingly soluble in water; when boiled with water for several days, it yields hydroxyvalerolactone (compare Fittig and Urban, this vol., p. 958) and a small quantity of levulinic acid.

F. S. K.

Decomposition of Dibromocaproic Acid. By R. Fittig and J. Hillert (*Annalen*, **268**, 67—71).—Dibromocaproic acid (hydrosorbic acid dibromide) is readily decomposed by sodium carbonate, yielding an oily bromolactone; when boiled with water for a long

time, it is converted into hydroxycaprolactone (compare Fittig and Hillert, this vol., p. 959), and *homolevulinic acid*,

$$CH_2Me\cdot CO\cdot CH_2\cdot CH_2\cdot COOH.$$

This acid melts at 32—33°, or possibly at a higher temperature, and is very readily soluble in water, alcohol, and ether. The *calcium* salt, $(C_6H_9O_3)_2Ca + 1\frac{1}{2}H_2O$, crystallises in colourless plates, and has been previously erroneously described as the calcium salt of hydroxyhydrosorbic acid (*Annalen*, **200**, 57). The *silver* salt, $C_6H_9O_3Ag$, separates from boiling water in crystals, and is only sparingly soluble.

F. S. K.

Tetrolic Acid. By R. Fittig and M. C. Clutterbuck (*Annalen*, **268**, 96—110).—The authors find that, contrary to the statement of Aronstein and Hollemann (Abstr., 1889, 878), an aqueous solution of tetrolic acid is not reduced by sodium amalgam in acid solution, either at the ordinary temperature or at 100°; tetrolic acid is slightly volatile with steam.

In examining the behaviour of tetrolic acid with bromine, the authors have arrived at results quite different from those of Lagermark (*Ber.*, **12**, 854), Pinner (*Ber.*, **14**, 1081), and Michael and Pendleton (Abstr., 1888, 1176). When a carbon bisulphide solution of tetrolic acid is treated with the molecular quantity of bromine, under the conditions described by Fittig in the case of angelic acid (Abstr., 1891, 39), hydrogen bromide is evolved in large quantities, and a comparatively small quantity of a yellowish-brown, semi-solid substance is produced, but no well-defined compound can be isolated. In chloroform solution, however, other conditions remaining the same, the tetrolic acid is converted almost quantitatively into dibromocrotonic acid, only traces of hydrogen bromide are evolved, and the sole bye-product is a very small quantity of an oil having a very irritating odour.

Dibromocrotonic acid, $C_4H_4Br_2O_2$, separates from chloroform in transparent, monosymmetric crystals, $a : b : c = 1{\cdot}1907 : 1 : 1{\cdot}6692$, $\beta = 80°\ 55\frac{1}{2}'$, melts at 119·8—120·4°, and slowly volatilises at 100°; it is readily soluble in alcohol, ether, and warm chloroform, but more sparingly in light petroleum and hot water; it separates unchanged from boiling water in colourless needles. The *silver* salt, $C_4H_3Br_2O_2Ag$, crystallises from boiling water in transparent plates, and is very stable in the light. The *barium* salt, $(C_4H_3Br_2O_2)_2Ba + 3H_2O$, is readily soluble in boiling water, from which it crystallises in small prisms. When dibromocrotonic acid is treated with sodium amalgam in cold dilute sulphuric acid solution, it is converted into tetrolic acid, no crotonic acid being formed. It is only very slowly acted on by bromine at 100°, in chloroform solution, yielding hydrogen bromide, and a small quantity of *tribromocrotonic acid*, $C_4H_3Br_3O_2$; the last-named compound separates from chloroform in colourless, feathery crystals, and melts at 131·5—132°.

Tetrolic acid combines with concentrated hydrobromic acid at the ordinary temperature, yielding a monobromocrotonic acid, $C_4H_5BrO_2$, which crystallises from light petroleum in feathery plates, melts at 93·5°, and differs in appearance and in other physical properties from

the bromocrotonic acid (m. p. 91°) prepared by Kolbe from $\alpha\beta$-dibromobutyric acid (compare Michael and Brown, *Amer. Chem. J.*, **9**, 277). The barium salt of the acid (m. p. 93·5°) crystallises in plates containing 2 mols. H_2O, whereas that of the isomeride (m. p. 91°) forms prismatic needles containing $3\frac{1}{2}$ mols. H_2O. F. S. K.

Some New δ-Lactones. By R. Fittig and C. Christ (*Annalen*, **268**, 110—129).—*Ethyl α-ethylacetoglutarate*,

$$COOEt\cdot CEtAc\cdot CH_2\cdot CH_2\cdot COOEt,$$

can be obtained by treating ethyl sodethylacetoacetate with ethyl β-iodopropionate in alcoholic solution; it is a yellow liquid, and cannot be distilled even under reduced pressure.

γ-Ethyl-γ-acetobutyric acid, $CHEtAc\cdot CH_2\cdot CH_2\cdot COOH$, prepared by hydrolysing the preceding compound with dilute hydrochloric acid, is a thick, very hygroscopic oil, boiling at 173—174° under a pressure of 10 mm., and at 279—281° with slight decomposition under the ordinary atmospheric pressure; it is soluble in about 18 times its volume of water at the ordinary temperature, and is miscible with alcohol and ether in all proportions. The *barium* salt, $(C_8H_{13}O_3)_2Ba$, crystallises from hot alcohol in slender, lustrous needles, is very hygroscopic, and dissolves freely in water. The *calcium* salt, $(C_8H_{13}O_3)_2Ca$, separates from alcohol in small, colourless, nodular crystals, and is very readily soluble in water. The *silver* salt, $C_8H_{13}O_3Ag$, is a colourless compound, moderately easily soluble in cold water; it turns reddish on exposure to light.

γ-Ethyl-δ-caprolactone, $\begin{matrix}CHMe\cdot CHEt\\ |\\ O-CO-CH_2\end{matrix}>CH_2$, is formed when ethylacetobutyric acid is reduced with sodium amalgam, and the product boiled with dilute hydrochloric acid for a short time. It is a colourless, transparent, mobile liquid, boils at 254—255°, and has a sp. gr. of 1·0804, 20°/4°; it is miscible with alcohol and ether in all proportions, and is soluble in 28 times its volume of water at the ordinary temperature, separating again from the solution on the addition of sodium carbonate. It is volatile with steam, and in its behaviour with boiling water it resembles Wolff's δ-caprolactone (*Annalen*, **216**, 127), equilibrium being established when the solution contains about 33 parts of lactone to 67 parts of acid.

Barium ethyl-δ-hydroxycaproate, $(C_8H_{15}O_3)_2Ba$, prepared by boiling the lactone with barium hydroxide, separates from cold water in colourless crusts, and is only sparingly soluble in cold water, and almost, or quite, insoluble in alcohol. The *calcium* salt, $(C_8H_{15}O_3)_2Ca$, forms colourless, nodular crystals, and is only sparingly soluble in cold water, and almost insoluble in alcohol. The *silver* salt, $C_8H_{15}O_3Ag$, forms moss-like crystals, and dissolves freely in hot water.

Ethyl α-benzylacetoglutarate,

$$COOEt\cdot CAc(CH_2Ph)\cdot CH_2\cdot CH_2\cdot COOEt,$$

was prepared by treating ethyl sodiobenzylacetoacetate with ethyl β-iodopropionate in alcoholic solution, but it was not obtained in a state of purity; on boiling the crude product with dilute hydrochloric

acid, *benzylacetoglutaric* acid is obtained as a thick, yellow oil, boiling at 254—256° under a pressure of 20 mm.

γ-Benzyl-δ-caprolactone, $C_{13}H_{16}O_2$, is formed in very small quantities when benzylacetoglutaric acid is reduced with sodium amalgam; it crystallises in small needles, melts at 54—56° (probably at a higher temperature), boils at 216—218° under a pressure of 15 mm., and is very readily soluble in alcohol and ether, but more sparingly in light petroleum, and only very sparingly in cold water, the aqueous solution remaining neutral, even after having been warmed. *Barium benzylhydroxycaproate*, $(C_{13}H_{17}O_3)_2Ba$, prepared by boiling the lactone with barium hydroxide, separates from alcohol in colourless, ill-defined crystals.

Ethyl dibenzylacetoacetate has been described by Ehrlich (*Annalen*, **187**, 24) as a yellow oil; it separates from light petroleum in well-defined, transparent crystals, melts at 57°, boils at 230—234° under a pressure of 12 mm., and is very readi y soluble in alcohol and ether, but more sparingly in light petroleum. The corresponding acid, $C_{16}H_{16}O_2$, separates from light petroleum in crystals, and melts at 89°, not at 85°, as stated by Sesemann (*Ber.*, **6**, 1085; and **10**, 785).

F. S. K.

Ethyl Chlorocarbonate. By B. Pawlewski (*Ber.*, **25**, 1449—1451).—Pure ethyl chlorocarbonate boils at 93·1° under 760 mm. pressure. Its sp. gr. is 1·14396 at 15°, and was determined in a dilatometer of special form; the number obtained by Dumas for this constant is 1·133. The author gives a table showing the specific gravity and coefficients of expansion at temperatures between 0° and 90°. The curve showing the rate of change of the coefficient of expansion shows points of inflexion at 40° and 80°. The observed molecular refraction $R_M = 37{\cdot}98$, whilst the calculated value is 37·66. The vapour density was determined in a V. Meyer apparatus between 100° and 277°. The vapour density of the substance is normal at temperatures below 250°; above that temperature, decomposition into ethyl chloride and carbonic anhydride occurs gradually, not suddenly, as generally stated.

W. J. P.

Preparation of Maleïc Anhydride. By J. Volhard (*Annalen*, **268**, 255—256).—Maleïc anhydride can be conveniently prepared by gently heating an intimate mixture of fumaric acid (2 mols.) and phosphorus oxychloride (1 mol.) until the evolution of hydrogen chloride ceases, and then distilling the anhydride; the yield is about 84 per cent. of the theoretical, and any phosphorus oxychloride in the product can be easily got rid of by redistilling. Phosphoric anhydride may be employed in the place of phosphorus oxychloride; the yield is very good in this case also.

F. S. K.

β-Methylmalic Acid. By W. Wislicenus (*Ber.*, **25**, 1484—1488; compare this vol., p. 589).—Specimens of β-methylmalic acid, prepared from the pure sodium salt (see below), may be obtained in crystals which melt at 119—120°. The *sodium salt*, $C_5H_6O_5Na_2 + 1\frac{1}{2}H_2O$, is formed by neutralising the acid with soda, or by the action of sodium ethoxide on the ethyl sodium salt; on adding boiling

alcohol to its aqueous solution, it is deposited in colourless crystals. The *silver*, *lead*, and *mercurous salts* are amorphous, and insoluble in water. The *barium salt*, $C_5H_6O_5Ba + 2\frac{1}{2}H_2O$, crystallises from water in small, colourless, lustrous plates. The *zinc salt* crystallises from water with 6 mols H_2O in lustrous prisms. β-Methylmalic acid yields mesaconic acid and citraconic acid when heated in a current of dry air at 170°.

A comparison of the properties of citromalic acid and α-methylmalic acid shows that these compounds are identical. J. B. T.

Aqueous Solutions of Tartaric and Racemic Acids. By L. Marchlewski (*Ber.*, **25**, 1556—1562).—Berthelot and Jungfleisch observed no thermic effect on mixing solutions of dextro- and lævo-tartaric acids, and Jahn subsequently confirmed this, employing 4 per cent. solutions. Ostwald found that solutions of tartaric and racemic acids have the same conductivity for all dilutions; assuming, therefore, that dextro- and lævo-tartaric acids have similar properties, racemic acid must in solution be dissociated into its components, at any rate in the concentrations investigated by Ostwald. Raoult examined the cryoscopic behaviour of solutions of tartaric and racemic acids, and concluded that in a solution containing 14·229 grams of racemic acid dissolved in 100 grams of water 1·037 grams of non-dissociated racemic acid existed, whilst in one containing 7·627 grams of racemic acid dissolved in 100 grams of water only 0·227 gram of the non-dissociated compound existed. The author has made a series of accurate determinations of the specific gravity of solutions of tartaric and racemic acids. He finds that the specific gravities of solutions of the two acids exhibit close agreement up to a concentration of 10 per cent. The following table illustrates his results above this concentration:—

Percentage of tartaric or racemic acid in solution.	Specific gravity of tartaric acid solution.	Specific gravity of racemic acid solution.	Specific volume of tartaric acid solution, d_1.	Specific volume of racemic acid solution, d_2.	$d_1 - d_2$.
10·666	1·04950	1·04969	0·95283	0·95266	0·00017
14·018	1·06600	1·06623	0·93809	0·93788	0·00021

Racemic acid solutions of a concentration 10—14 per cent. have therefore a smaller specific volume than those of tartaric acid of the same concentration, and it would appear that on mixing solutions of dextro- and lævo-tartaric acid of this concentration a contraction and thermic reaction occur. The specific gravities of 4 per cent. solutions of dextro- and lævo-tartaric acids were found to be 1·01770 and 1·01767 respectively, and therefore, within the limits of experimental error, identical. The solutions were then mixed, and gave in two determinations 1·01769 and 1·01766, showing that no alteration of volume had taken place. All the specific gravities were compared with water at 4° and reduced to a vacuum. A. R. L.

Tartrotartaric Acid. By M. E. Mulder (*Rec. Trav. Chim.*, **10**, 171—210).—By the action of ethyl chloride on ethyl disodium tartrate, two chief products are obtained, the one (*a*) soluble in alcohol, absolute ether, and ethyl chloride, the other (*b*) insoluble in these solvents. The soluble product is of a bright yellow colour, and has not been obtained in the pure state; the insoluble substance is an almost colourless solid. By the action of hydrogen chloride on these compounds dissolved or suspended in ethyl chloride, carbonic anhydride is eliminated, and thick liquid products are obtained apparently of the same composition. The aqueous solution of this product gives a cherry-red coloration with ferric chloride.

The aqueous solution of *a* does not give precipitates with aqueous solutions of copper sulphate, acetate, or chloride, with zinc sulphate or acetate, or with mercuric chloride or silver nitrate, but yields precipitates with calcium chloride and lead acetate. The same result is obtained with alcoholic solutions with the exceptions that lead acetate gives no precipitate and silver nitrate gives a reddish-brown coloration and afterwards a reddish-brown precipitate. With alcoholic solutions in presence of water, all these salts give precipitates.

An aqueous solution of *b* is not precipitated by cupric chloride; an alcoholic solution of cupric chloride gives an amorphous cupric compound with *b* insoluble in alcohol.

An alcoholic solution of the product *a* gives no precipitate with alcoholic cupric chloride, but, if the mixture is added to water, a substance is obtained which crystallises in prismatic needles of a bright green colour, soluble in alcohol or ether and almost insoluble in water. It gives a cherry-red coloration with ferric chloride, and a bluish-green solution with sodium hydroxide. Its formula is $C_{16}H_{24}CuO_{11}$; from its synthesis it must be ethyl ethylcoppertartrotartrate,

$$\begin{array}{l} COOEt\cdot CH-C(COOEt)\cdot CO\cdot CH(OEt)\cdot CH(OH)\cdot COOEt. \\ \quad\quad\quad\

β-Methylamidocrotonanilide (Knorr and Taufkirch, this vol., p. 708) crystallises in colourless prisms, melts at 145°, and is very similar in solubility to β-amidocrotonanilide. A. G. B.

Derivatives of Thiocarbamide and Carbamide. By O. Probst (*J. pr. Chem.* [2], **45**, 416).—When phenylhydrazine acts on thiohydantoic acid, or, more simply, when an alcoholic solution of thiocarbamide, chloracetic acid, and phenylhydrazine is warmed, a *compound*, $C_9H_9N_3OS$, is formed; this crystallises in monoclinic prisms, and melts with decomposition at 175°.

Pinner's phenylurazole is easily formed by heating ethyl allophanate with phenylhydrazine. A. G. B.

Thiophenchlorophosphine and its Derivatives. By H. Sachs (*Ber.*, **25**, 1514—1518).—*Thiophenchlorophosphine*, $C_4SH_3{\cdot}PCl_2$, is obtained by passing the mixed vapours of thiophen and phosphorus chloride through a hard, glass tube packed with pieces of pumice and heated to a dull red heat. After continuing the treatment for eight days, 14 grams were obtained from 100 grams of thiophen, and 60 grams of thiophen were recovered. It boils at 218°, and is decomposed by water, yielding hydrochloric and thiophenphosphinous acids. It greatly resembles phosphenyl chloride, $C_6H_5{\cdot}PCl_2$. The PCl_2 group is probably in the 2-position.

Thiophentetrachlorophosphine, $C_4SH_3{\cdot}PCl_4$, is obtained by the addition of chlorine to the dichlorophosphine. It is a solid substance resembling phosphoric chloride, and is decomposed by water into the oxychloride and finally the phosphinic acid.

Thiophenoxychlorophosphine, $C_4SH_3{\cdot}POCl_2$, is best prepared by passing dry sulphurous anhydride over the tetrachloride, and distilling the resulting mixture of oxychlorophosphine and thionyl chloride. It boils at 258—260°.

Thiophenphosphinous acid, $C_4H_3S{\cdot}PO_2H_2$, is formed when the dichlorophosphine is decomposed with water. It forms needles melting at 70°, and is analogous in its properties and reactions to phenylphosphinous acid.

Thiophenphosphinic acid, $C_4SH_3{\cdot}PO(OH)_2$, is obtained by decomposing the tetrachlorophosphine with water. It crystallises from water in very small, short needles, melts at 159°, dissolves readily in water, alcohol, and ether, and is insoluble in water. It resembles phenylphosphinic acid. The *silver salt*, $C_4H_3S{\cdot}PO(OAg)_2$, forms a white precipitate which dissolves both in ammonia and in nitric acid.

Thiophendiethylphosphine. $C_4SH_3{\cdot}PEt_2$, is obtained by treating the dichlorophosphine with zinc ethyl in ethereal solution. It forms a colourless or light-yellow liquid boiling at 225° and having a phosphine-like odour. It unites with methyl iodide, best in ethereal solution, forming *thiophendiethylmethylphosphonium iodide*,

$$C_4SH_3{\cdot}PEt_2MeI,$$

as a white powder melting at 122°, and dissolving in alcohol and water, but not in ether. The chloride of the base forms a *platino-*

chloride, $(C_4SH_3{\cdot}PEt_2Me)_2PtCl_6$, a crystalline, yellow powder. Thiophentriethylammonium iodide can also be prepared, but not so easily as the diethylmethyl compound. C. F. B.

Action of Sulphuric Acid on Hydrocarbons with a Closed Chain. By Maquenne (*Compt. rend.*, **114**, 918—920).—Renard has stated that heptine, C_7H_{12}, is rapidly attacked by strong sulphuric acid with production of two isomerides $C_{14}H_{24}$, and a new hydride C_7H_{14}. The author has prepared pure heptine by the action of alcoholic potash on the nitrosochloride, $C_7H_{12}NOCl$. When agitated with its own volume of sulphuric acid of 66°, part dissolves with development of heat and evolution of sulphurous anhydride, whilst another part forms a layer of supernatant liquid which can be decanted off and distilled. The chief product is a hydrocarbon C_7H_{14}, which, after distillation over sodium, boils at 94—96°.

The unsaturated hydrocarbons derived from camphoric acid are attacked by strong sulphuric acid in much the same way as heptine. The hydrocarbon, C_8H_{14}, obtained by the destructive distillation of copper camphorate, is converted, under similar conditions, into xylene hexahydride, and this is true also of the hydrocarbon, C_8H_{14}, obtained by the destructive distillation of silver camphorate.

The hydration may be due to the sulphurous anhydride which is evolved as a product of the decomposition of part of the original hydrocarbon. C. H. B.

Halogen Derivatives of Methylbenzenes. By A. Töhl (*Ber.*, **25**, 1521—1526).—*Iodomesitylene*, $C_6H_2Me_3I$ [$Me_3 : I = 1 : 3 : 5 : 6$], can be obtained from mesitylene and iodine in the presence of mercuric oxide, but is best prepared from mesidine by the diazo-reaction. It forms highly refracting crystals, melts at 30·5°, and boils at 248—250°.

Iododurene, C_6HMe_4I [$Me_4 : I = 1 : 2 : 4 : 5 : 6$], was obtained by adding durene and mercuric oxide to iodine in light petroleum allowing the mixture to remain for three weeks, and finally heating on the water-bath. It melts at 80°, boils at 285—290°, and dissolves readily in light petroleum, from which it crystallises in ill-defined prisms or in lustrous needles. It is better prepared by fusing together durene and iodine, and adding mercuric iodide until the iodine disappears.

When durene is dissolved in light petroleum, a little iodine added, and chlorine passed in, *dichlorodurene* separates out, and *monochlorodurene* remains dissolved. The latter melts at 48°, boils at 237—238° (uncorr.), and crystallises from alcohol in large, transparent tables. The former melts at 189—190°, boils at 275° (uncorr.), and dissolves in carbon bisulphide, chloroform, and carbon tetrachloride, sparingly in alcohol and light petroleum.

When prehnitene, $C_6H_2Me_4$ [$Me_4 = 1 : 2 : 3 : 4$], obtained from pentamethylbenzene and sulphuric acid, is chlorinated, it yields *monochloroprehnitene*, an oil boiling at 240° (uncorr.), and *dichloroprehnitene*, which melts at 195°, boils at 280°, and crystallises from chloroform in highly refracting prisms.

Chloropentamethylbenzene, C_6Me_5Cl, was prepared by chlorinating a solution of pentamethylbenzene in light petroleum. It melts at 155°, crystallises from light petroleum in ill-defined, apparently monoclinic prisms, from alcohol, in which it is but sparingly soluble, in plates, and is very slightly volatile with steam.

Several fluoromethylbenzenes were prepared by decomposing the corresponding diazopiperidides, themselves obtained from amido-derivatives, with strong hydrofluoric acid. Their melting points are but little higher than those of the hydrocarbons from which they are derived. *Fluorometaxylene*, $C_6H_3Me_2F$ [$Me_2 : F = 1 : 3 : 4$], boils at 143°, *fluoromesitylene* at 171—172°, while *fluoropseudocumene*, $C_6H_2Me_3F$ [$Me_3 : F = 1 : 2 : 4 : 5$], melts at 26°, and boils at 172°.

C. F. B.

Action of Sulphuric Acid on Monobromoprehnitene. By A. Töhl (*Ber.*, **25**, 1526—1527).—*Monobromoprehnitene* was prepared by adding an acetic acid solution of bromine to an acetic acid solution of prehnitene (prepared from pentamethylbenzene). It crystallises from light petroleum in large, transparent tables, melts at 30°, and boils at 265°. When allowed to remain with sulphuric acid in a warm place, it is completely decomposed in two days; solid dibromoprehnitene, melting at 210°, is formed, and the liquid contains prehnitenesulphonic acid. 2 mols. of monobromoprehnitene have thus, under the influence of sulphuric acid, yielded 1 mol. of prehnitene and 1 mol. of dibromoprehnitene.

C. F. B.

Action of Sulphuric Acid on Chlorodurene. By A. Töhl (*Ber.*, **25**, 1527—1530).—When monochlorodurene is heated for several hours at 60° with concentrated sulphuric acid, the mixture being frequently shaken, some solid chloropentamethylbenzene, melting at 155°, separates out, and in the solution is found the sulphonic acid of a chlorotrimethylbenzene, probably chloropseudocumene. $C_6H_2Me_3Cl$ [$Me_3 : Cl = 1 : 2 : 4 : 3$]. The *barium*, $(C_9H_{10}Cl{\cdot}SO_3)_2Ba + H_2O$, *sodium*, $C_9H_{10}Cl{\cdot}SO_3Na + \frac{1}{2}H_2O$, and *potassium*, $C_9H_{10}Cl{\cdot}SO_3K + H_2O$, *salts* of this acid were prepared. By the action of hydrochloric acid at 180° on this acid, a chlorotrimethylbenzene, melting at 213°, was obtained; this gave a dinitro-derivative which, on reduction, yielded an amido-derivative exhibiting the reactions of an orthodiamine. The chlorotrimethylbenzene was, therefore, probably the chloropseudocumene mentioned above. Sulphuric acid has thus converted 2 mols. of chlorodurene into 1 mol. of chloropentamethylbenzene and 1 mol. of chloropseudocumene, a "migration" of a methyl group having taken place, and not of the halogen atom, as is usually the case.

C. F. B.

Symmetrical and Unsymmetrical Ethylmetaxylene. By A. Töhl and A. Geyger (*Ber.*, **25**, 1533—1539).—When metaxylene is treated with ethyl bromide and aluminium chloride, both unsymmetrical and symmetrical ethylmetaxylene are formed, and are separated by means of their sulphonamides, which melt at 147—148° and 127—128° respectively. After these have been separated, there remains an uncrystallisable sulphonamide from which, by heating

with strong hydrochloric acid at 180°, a hydrocarbon can be obtained which boils at 183—185°, and is oxidised by nitric acid to paraxylylic acid [$Me_2 : COOH = 1 : 2 : 4$]; this acid, when distilled with lime, yields orthoxylene, so that the sulphonamide must have been derived from ethylorthoxylene, $C_6H_3Me_2Et$ [$Me_2 : Et = 1 : 2 : 4$], which had been formed from metaxylene and ethyl bromide, the aluminium chloride bringing about a molecular transformation. The symmetrical ethylmetaxylene was also prepared from symmetrical bromoxylene and ethyl bromide; it boils at 186°, and yields a dibromo-derivative melting at 216—217°, and a dinitro-derivative melting at 234—235°.

Unsymmetrical ethylmetaxylene, $C_6H_3Me_2Et$ [$Me_2 : Et = 1 : 3 : 4$], yields, with bromine, *monobromethylxylene*, $C_6H_2Me_2EtBr$ [$Me_2 : Et : Br = 1 : 3 : 4 : 6$]. This boils at 247—248°, and its constitution is proved by the fact that, when oxidised, it yields the bromoxylylic acid melting at 172—173°, which can be obtained by oxidising the solid bromopseudocumene. *Mononitroethylxylene*, obtained by dissolving the hydrocarbon in cold, strong nitric acid, boils at 270—272°, and when reduced with iron and acetic acid, yields *amidoethylxylene*, a colourless oil boiling at 144—145° under 20 mm. pressure, and turning brown in the air. The *sulphate* of this base, $(C_{10}H_{15}N)_2,H_2SO_4 + H_2O$, forms white plates, which turn red when exposed to light. The base is known to have the symmetrical constitution [$Me_2 : Et : Br = 1 : 3 : 4 : 6$], because, when the amido-group is displaced by bromine, and the resulting compound oxidised, bromoxylylic acid [$Me_2 : COOH : Br = 1 : 3 : 4 : 6$], melting at 172—173°, is formed. The *sulphonic acid* has the constitution [$Me_2 : Et : SO_3H = 1 : 3 : 4 : 6$], as the sulphonamide melting at 148°, when oxidised with alkaline permanganate, yields a sulphaminic acid [$Me_2 : COOH : SO_2{\cdot}NH_2 = 1 : 3 : 4 : 6$], identical with that obtained by oxidising pseudocumene-sulphonamide.

Symmetrical ethylmetaxylene [$Me_2 : Et = 1 : 3 : 5$] was obtained from the sulphonamide melting at 128°. This has the constitution [$Me_2 : Et : SO_2{\cdot}NH_2 = 1 : 3 : 5 : 2$], since the sulphaminic acid obtained by oxidising it with permanganate yields mesitylenic acid when heated with hydrochloric acid, and is identical with the sulphaminemesitylenic acid [$Me_2 : COOH : SO_2NH_2 = 1 : 3 : 5 : 2$] melting at 276°. The hydrocarbon, when treated with bromine in the presence of iodine, yields monobromethylxylene [$Me_2 : Et : Br = 1 : 3 : 5 : 2$], which, when oxidised, yields the bromomesitylenic acid [$Me_2 : COOH : Br = 1 : 3 : 5 : 2$] melting at 214°. This monobromethylxylene, when heated with chlorosulphonic acid, yields the *sulphonic acid* [$Me_2 : Et : Br : SO_3H = 1 : 3 : 5 : 2 : 6$], whose *barium*, $(C_{10}H_{12}Br{\cdot}SO_3)_2Ba + 4H_2O$, and *cadmium* (with $3H_2O$) *salts* crystallise in plates, sparingly soluble in water. The sodium salt of this acid was treated with zinc-dust and ammonia to remove the bromine; the *barium salt*, $(C_{10}H_{13}{\cdot}SO_3)_2Ba + 6H_2O$, of the *ethylxylenesulphonic acid* [$Me_2 : Et : SO_3H = 1 : 3 : 5 : 6$] thus obtained crystallises in needles; the *sulphonamide* in white plates melting at 116—117°. The second *bromethylxylenesulphonic acid* [$Me_2 : Et : Br : SO_3H = 1 : 3 : 5 : 6 : 2$] was obtained by treating the sodium salt of the above-mentioned ethylxylenesulphonic acid [$Me_2 : Et : SO_3H =$

1 : 3 : 5 : 2] with bromine; the *calcium salt*, $(C_{10}H_{12}Br{\cdot}SO_3)_2Ca + 6H_2O$, crystallises in lustrous plates; the sulphonamide in yellowish needles melting at 156°. C. F. B.

Sodium Phenyl Sulphite. By C. Schall (*Ber.*, **25**, 1490).—By the action of sulphurous anhydride on anhydrous sodium phenoxide at ordinary temperatures, the author has prepared a compound which he believes to be unsymmetrical sodium phenyl sulphite, $NaSO_2{\cdot}OPh$. J. B. T.

Action of Bleaching Powder and of Hypochlorous Acid on Quinones. By T. Zincke (*Ber.*, **25**, 1493—1497; compare this vol., pp. 720 and 859).—Isocoumarincarboxylic acid, $C_6H_4<\begin{matrix}CO{\cdot}O\\ |\\ CH{:}C{\cdot}COOH\end{matrix}$, has recently been prepared by Bamberger and Kitschelt (this vol., p. 882); it may also be obtained by heating the acid $C_{10}H_8O_5$ for some time at 225—230°. The *methyl salt* crystallises from methyl alcohol in slender, lustrous needles melting at 172—173°.

Isocarbostyrilcarboxylic acid, $C_6H_4<\begin{matrix}CO{\cdot}NH\\ |\\ CH{:}C{\cdot}COOH,\end{matrix}$ can be obtained by the action of ammonia (25 per cent.) on the acid $C_{10}H_8O_5$ at 160—170°; the product is pure and the reaction proceeds quantitatively; on heating with zinc dust in excess, isoquinoline is formed. J. B. T.

Fluorescein. By R. Meyer and H. Hoffmeyer (*Ber.*, **25**, 1385—1390; see also Abstr., 1891, 1029).—The phenolphthalein anhydride obtained by Baeyer in the preparation of phenolphthalein has been further examined by the authors. They propose to name it fluoran, and consequently fluorescein would be a dihydroxyfluoran.

Fluoran, $\begin{matrix}CO{\cdot}O\\ |\\ C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>O$, crystallises with ½ mol. of alcohol, melts at 180°, and gives a dibromide melting at 254—258°. The authors have attempted to convert fluoran into fluorescein, or *vice versâ*, without success. They have, however, obtained the same acid, of the formula $C_{20}H_{14}O_3$, from both compounds.

In the hope of obtaining fluoran, fluorescein chloride was treated with reducing agents; a large quantity of unaltered material was obtained, together with compounds containing chlorine.

Phosphorus pentabromide acts on fluorescein in a similar way to the pentachloride; the product was not obtained pure, and, on analysis, gave numbers corresponding with a tribromofluoran, $C_{20}H_9Br_3O_3$. It crystallises from xylene in yellowish, microscopic needles, and melts at 298—300°. The bromide (15 grams) is boiled for 24 hours in a reflux apparatus with sodium hydroxide (60 grams), absolute alcohol (600 c.c.), and excess of zinc dust, and the product filtered, diluted with water, and the alcohol distilled off. An oily product is thus obtained, which dissolves in a large quantity of hot water, and, on acidifying with hydrochloric acid, the acid $C_{20}H_{14}O_3$ is precipitated. The latter is identical with the phenol-

phthalin anhydride obtained by Baeyer by reducing phenolphthaleïn anhydride with zinc dust.

By reducing fluoran in a similar way, the same acid is obtained. The authors give the formula $COOH{\cdot}C_6H_4{\cdot}CH{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}O$ to this acid. It crystallises from alcohol in rhombic prisms or tablets, melts at 226—228° (uncorr.), and dissolves in concentrated sulphuric acid with a yellow coloration; on warming, the solution turns cherry-red, and, on adding water, gives a brown precipitate which dissolves in ether with a yellowish-green fluorescence. E. C. R.

Dinitrosacyls. By A. F. Holleman (*Rec. Trav. Chim.*, **10**, 211—222; compare Abstr., 1889, 49).—Dinitrosacyls have the following properties:—

Alkalis dissolve them with a yellow colour; mineral acids precipitate the corresponding acids from the solution. They are dissolved by sulphuric acid with a reddish-brown colour, and, on the addition of water, the corresponding acids are obtained. With aniline or its homologues, the corresponding anilide is obtained. $(R{\cdot}CO{\cdot}CNO)_2$ yields $R{\cdot}CO{\cdot}NHR_1$. The substitution of the nitroso-group for hydrogen in the group $\cdot CO{\cdot}CH_3$ weakens the combination between the carbon atoms. By reduction with zinc powder and acetic acid, the dinitrosacyls lose nitrogen and give diketones. Boiling with concentrated hydrochloric acid causes dinitrosacyls to give acids of the type R·COOH, together with oxalic acid, ammonia, and hydroxylamine.

Dinitrosacyls may be prepared by the oxidation of isonitrosoketones.

Attempts to prepare dinitrosacyls of the fatty series by the action of nitric acid on isonitrosoacetone and on isonitrosomethyl hexyl ketone have not been successful. Fine crystals of the hexyl ketone compound were prepared by Claisen's method (*Ber.*, **20**, 252; **22**, 526). They melt at 59°.

It is yet doubtful whether the formula of the isonitrosomethylhexyl ketone should be $C_6H_{13}{\cdot}CO{\cdot}CH{\cdot}NOH$ or $C_5H_{11}{\cdot}C(NOH){\cdot}CO{\cdot}CH_3$, as caproic acid is obtained on oxidising it with nitric acid, but no acetic acid is produced.

Dianisyldinitrosacyl.—Paracetylanisoïl is prepared by Gattermann's method. Resinification is avoided when 20 grams of anisoïl react with 25 grams of acetic chloride dissolved in 150—200 c.c. of carbon bisulphide. It melts at 38°.

Acetylanisoïl, in portions of 5 grams at a time, is introduced into a mixture of 50 grams of nitric acid of sp. gr. 1·4 with 5 grams of concentrated sulphuric acid and carefully heated. The dianisyldinitrosacyl which separates, after being washed with water and purified with acetic acid, melts at 138—139°. The yield is about 70 per cent. of the ketone used. Anisic acid is obtained from the alkaline and acid solutions. Reduction by zinc powder and acetic acid yields symmetrical dianisoylethane; 25 c.c. of glacial acetic acid diluted with 10 c.c. of water is raised to the boiling point, and zinc powder added in small portions with 1 gram of the dinitrosacyl in concentrated acetic solution; after each addition, the liquid is boiled until colourless. Water gives a

flocculent precipitate of the diketone; it is purified by extraction with boiling alcohol and crystallisation from glacial acetic acid. It crystallises in fine plates melting at 154°. By boiling with ammonium acetate solution, it yields α-α'-dianisylpyrroline, which crystallises from a mixture of alcohol and acetic acid in thin plates melting at 223°. This derivative dissolves in sulphuric acid with a reddish-brown colour, changing to intense, bluish-violet on heating.

Dianisyldinitrosacyl is also obtained by oxidation of sodiumisonitrosoacetylanisoïl with nitric acid. By the action of aniline on dianisyldinitrosacyl, two well-crystallised compounds are obtained. The anilide of anisic acid melts at 170°. The other compound is obtained in dark-brown needles, becoming white on purification; it is now under investigation.

Diparethoxydiphenylenedinitrosacyl. — Paracetylphenetoïl, which melts at 36—37° and not at 61°, is oxidised in like manner to the acetylanisoïl. The diparethoxydiphenylenedinitrosacyl fuses at 131° and yields, on reduction with zinc powder and acetic acid, diparethoxydiphenylenethylene diketone fusing at 132°. This compound gives 2 : 5-diparethoxydiphenylenepyrroline melting at 210°.

Dinaphthyldinitrosacyl was not obtained on oxidation of β-naphthyl methyl ketone with nitric acid of sp. gr. 1·4. Although some of the dinitrosacyl reactions were obtained with the mass resulting from the oxidation of sodiumisonitrosomethylnaphthyl ketone, the substance itself has not been isolated. W. T.

The Oxymethylene Group in Isosafrole. By G. Ciamician and P. Silber (*Ber.*, **25**, 1470—1477).—A mixture of isosafrole (10 grams), potash (10 grams), and methyl alcohol (10 c.c.), when heated in a closed tube for 6—8 hours at 160—170°, is converted into a viscid liquid with evolution of a little hydrogen. The product is extracted with ether; on evaporating the ethereal solution, a yellowish liquid remains, which, on repeated distillation under reduced pressure, yields a substance which boils at 173° under 16 mm. pressure. This compound has the composition $OH{\cdot}C_6H_3(OCH_2{\cdot}OMe){\cdot}C_3H_5$, the methyl alcoholic potash having acted on the isosafrole as potassium methoxide.

On heating the phenol (22 grams) with methyl iodide (15 grams), potash (6 grams), and methyl alcohol (40 c.c.) under pressure on the water-bath for many hours, and evaporating the alcohol, a product is obtained which, on treatment with potash, partly dissolves. The soluble portion is a black, tarry mass, which is decomposed by distillation. The part insoluble in potash is dissolved in ether and the ethereal solution evaporated, when a substance is obtained which boils at 184—185° under 20 mm. pressure, and with slight decomposition at 285° under ordinary pressures; it is a thick, colourless, tasteless liquid, giving analytical numbers agreeing with the formula $OMe{\cdot}C_6H_3(O{\cdot}CH_2{\cdot}OMe){\cdot}C_3H_5$, but this constitution is given with reserve. On suspending it (7·5 grams) in hot water (600 c.c.) containing a little potash and adding a hot aqueous solution (1750 c.c.) of potassium permanganate (35 grams), oxidation occurs, and is completed by evaporation on the water-bath. Isovanillic acid may be

extracted from the residue, but other acids, including vanillic acid, are probably also produced.

When the phenolic compound, $OH{\cdot}C_6H_3(O{\cdot}CH_2{\cdot}OMe){\cdot}C_3H_5$ (22 grams), is heated for six hours in a reflux apparatus with acetic anhydride (60 grams) and anhydrous sodium acetate (10 grams), it gives a product which, after evaporation of the acetic anhydride, is digested with dilute soda. The residue is extracted with ether, and, on evaporation of the ethereal solution, an oil is obtained which, on distillation under diminished pressure, yields *diacetylmetapropenylcatechol*, $C_6H_3(OAc)_2{\cdot}C_3H_5$ $[(OAc)_2 : C_3H_5 = 4 : 3 : 1]$; this forms pearly scales, melts at 96·5°, and boils with slight decomposition at 305—308°. On oxidation with a hot aqueous solution of potassium permanganate, it yields diacetylprotocatechuic acid melting at 155—156°, not at 150—153°, as previously stated.

In the fractional distillation of the diacetylmetapropenylcatechol, an oil boiling at 306—307° is obtained which, on oxidation with hot potassium permanganate solution, yields a mixture of diacetyl- and monacetyl-protocatechuic acids. The latter forms white needles melting at 197—199°. It is soluble in ether, alcohol, hot ethyl acetate, and water. A little protocatechuic acid is obtained at the same time. W. J. P.

Azobenzene-, Hydrazobenzene-, and Benzidinedisulphonamide. By H. Limpricht and F. Meyer (*Annalen*, **268**, 130—142). —Azobenzenedisulphonamide, $NH_2{\cdot}\overset{2}{S}O_2{\cdot}C_6H_4{\cdot}\overset{4}{N}{:}\overset{4}{N}{\cdot}C_6H_4{\cdot}\overset{2}{S}O_2{\cdot}NH_2$, is easily obtained by oxidising the hydrazo-compound described below (compare, also, Mahrenholtz and Gilbert, *Annalen*, **202**, 336); it crystallises in yellow needles or prisms, melts at 305°, and is insoluble, or only very sparingly soluble, in most ordinary solvents, but readily soluble in boiling aniline. The *potassium* derivative, $C_{12}H_{10}N_4S_2O_4K_2$, crystallises in yellowish plates and prisms, and contains 2 mols. H_2O when dried over sulphuric acid. The *sodium* derivative,

$$C_{12}H_{10}N_4S_2O_4Na_2,$$

crystallises in microscopic plates, and after having been dried over sulphuric acid, loses 7 mols. H_2O at 150°.

Hydrazobenzenedisulphonamide $C_{12}H_{14}N_4S_2O_4$ (compare Mahrenholtz and Gilbert, *loc. cit.*), prepared by reducing metanitrobenzenesulphonamide, or the azo-compound just described, with zinc-dust and ammonia, crystallises from boiling 50 per cent. acetic acid in long, colourless needles, melts at 248°, and is almost insoluble in water, ether, chloroform, and toluene, and only sparingly soluble in alcohol, but readily in acetone and aniline. It dissolves in, and is decomposed by, warm, concentrated sulphuric acid, yielding a deep yellow solution, but it separates unchanged from concentrated ammonia; it reduces ammoniacal silver solutions and Fehling's solution on warming. The *potassium* derivative, $C_{12}H_{12}N_4S_2O_4K_2 + 1\frac{1}{2}H_2O$, crystallises in colourless needles or plates. The *sodium* derivative, $C_{12}H_{12}N_4S_2O_4Na_2 + 2\frac{1}{2}H_2O$, crystallises in small, colourless, concentrically-grouped needles.

Benzidinedisulphonamide, $NH_2 \cdot SO_2 \cdot C_6H_3(NH_2) \cdot C_6H_3(NH_2) \cdot SO_2 \cdot NH_2$, is formed, together with azobenzenedisulphonamide, amidobenzenesulphonamide, and a resinous base, the nature of which could not be determined, when hydrazobenzenedisulphonamide is heated with moderately concentrated hydrochloric acid for two to three days at 100°; it can also be prepared by warming the hydrazo-compound with stannous chloride. It crystallises from water in colourless, rhombic plates, and in long needles, melts at 278°, and is readily soluble in boiling acetone and boiling aniline, but only moderately easily in hot alcohol, and insoluble in ether, chloroform, and toluene; it dissolves in concentrated ammonia, yielding a yellow solution, from which a colourless, granular compound is precipitated on the addition of silver nitrate, and it is also readily soluble in dilute alkalis and dilute mineral acids. The *hydrochloride*, $C_{12}H_{14}N_4S_2O_4,2HCl$, crystallises in flat prisms which seem to contain 2 mols. H_2O after having been dried over sulphuric acid; it melts at 205°, and is readily soluble in water and alcohol. The *sulphate*, $C_{12}H_{14}N_4S_2O_4,H_2SO_4 + 2H_2O$, crystallises in prisms, and is readily soluble in water. F. S. K.

Oxyazo-compounds. By H. Goldschmidt and A. Pollak (*Ber.*, **25**, 1324—1347; see also Abstr., 1891, 1209).—Goldschmidt and Brubacher have shown that the acetyl and benzoyl derivatives of many hydroxyazo-compounds, when reduced with zinc-dust and acetic acid, yield acetanilide or benzanilide, and they maintain that this reaction is evidence that these compounds are hydrazones of quinones. The present paper deals with the reduction of other hydroxyazo-compounds, of disazo-compounds of the type of phenoldisazobenzene, of azo-compounds derived from resorcinol, and of the acetyl derivative of benzeneazoacetone.

Paratoluneneazoparacresol was converted into the *acetyl derivative* $C_6H_3MeO{:}N \cdot NAc \cdot C_6H_4Me$, and the latter reduced in alcoholic solution with zinc-dust and a few drops of acetic acid. After reduction, the excess of zinc-dust was filtered off, water added, and then dilute sulphuric acid, and the mixture extracted with ether. The ethereal solution contained paracetotoluidide; hence the reduction takes place in a similar way to that of the acetyl derivatives of other orthohydroxyazo-compounds. Benzoylparatolueneazoparacresol was reduced in the same way. An *hydrazo*-compound is first formed, and is precipitated on adding water. It melts at 144°, but is not pure. By further reduction, parabenzotoluidide is formed.

Parachlorobenzeneazoparacresol is obtained by the action of parachlorodiazobenzene chloride on an alkaline solution of paracresol. It crystallises from benzene in long, orange-red needles, and melts at 151—152°. The *acetyl* compound, obtained by the action of acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in long, reddish-yellow needles, and melts at 118—119°. The acetyl compound, on reduction, first yields *acetylparachlorobenzenehydrazoparacresol*, $OH \cdot C_6H_3Me \cdot NH \cdot NAc \cdot C_6H_4Cl$, which is obtained as follows:—The acetyl azo-compound in well cooled alcoholic solution is treated with zinc-dust and just enough acetic acid to decolorise the solution. The liquid is then filtered into a flask filled with

carbonic anhydride, and precipitated with water in the presence of a current of carbonic anhydride. The precipitate is quickly collected, dried on a porous plate, and crystallised from hot petroleum. It forms long, colourless, four-sided prisms, melts at 99° with a red coloration, and is soluble in ether, benzene, and petroleum. It is as little soluble in alkali as the other hydrazo-compounds obtained by Goldschmidt and Brubacher from acetylparahydroxyazo-compounds. When left for some time in contact with concentrated sodium hydroxide, it is converted into the primary hydroxyazo-compound. By the further reduction of acetylparachlorobenzeneazoparacresol, the molecule is split and acetoparachloranilide is obtained.

Benzoylparachlorobenzeneazoparacresol is obtained by boiling the hydroxyazo-compound, dissolved in benzene, with benzoic chloride. It crystallises in long, orange-red prisms, melts at 115°, and is easily soluble in benzene, but only sparingly in alcohol and petroleum. On reduction, it yields the hydrazo-compound,

$$OH\cdot C_6H_3Me\cdot NH\cdot NBz\cdot C_6H_4Cl;$$

this crystallises in colourless needles, melts at 172° with a red coloration, and is easily soluble in alcohol and benzene, sparingly so in light petroleum. It does not yield benzoparachloranilide on further reduction.

Metachlorobenzeneazoparacresol is obtained by the action of metachlorodiazobenzene chloride on a strongly alkaline solution of paracresol. It crystallises from hot, dilute alcohol in long, orange-red needles, melts at 103°, and is easily soluble in alcohol, benzene, and ether; very sparingly so in cold petroleum. The *acetyl* derivative crystallises from hot alcohol in orange-yellow prisms, melts at 73—74°, and is easily soluble in cold benzene and ether, and in hot alcohol and petroleum. On reduction, it first yields the *hydrazo*-compound, which crystallises in long, colourless needles, and melts at 92° with a red coloration. By further reduction, the molecule is split up and acetometachloranilide (m. p. 75°) is obtained.

Benzoylmetachlorobenzeneazoparacresol crystallises from hot alcohol in long, orange-red needles, melts at 90°, and is soluble in cold benzene and ether, and in hot alcohol and petroleum. On reduction, it yields an impure *hydrazo-compound* which melts at 127—128°, and is probably mixed with benzometachloranilide.

Benzeneazo-orthocresol, $C_6H_3MeO{:}N\cdot NHPh$ [Me : O : N·NHPh = 1 : 2 : 5], a paroxyazo-compound, has been examined in conjunction with the foregoing orthoxy-compounds. The acetyl derivative, on reduction, yields *acetylbenzenehydrazo-orthocresol*. The latter crystallises in colourless needles, melts at 88—89°, and turns yellow on exposure to air; it is insoluble in alkalis, but, by the prolonged action of alkalis, is converted into benzeneazo-orthocresol. The acetyl derivative does not yield amidocresol and acetanilide on further reduction.

Benzoylbenzeneazo-orthocresol, on reduction, yields a *hydrazo-compound* which is precipitated, on adding petroleum to its solution in benzene, in clusters of colourless needles; it melts at 142°. The decomposition of the benzoyl compound into amidocresol and benzanilide could not be effected.

From these results the authors conclude that the hydrazo-derivatives of hydroxyazo-compounds of the ortho-series, with a few exceptions, can be further reduced to amidophenols and an anilide: the compounds of the para-series cannot be so reduced. They are, however, so alike in other respects, that a similar constitution must be assigned to both.

Monoxydisazo-compounds.—Phenoldisazobenzene, the simplest representative of this class, if expressed as a quinone hydrazone, can be either a para- or ortho-quinone derivative, as shown by the formulæ:

$$CO<\begin{matrix}CH\text{———}CH\\ C(N_2Ph):CH\end{matrix}>C:N\cdot NHPh. \qquad CO<\begin{matrix}CH\text{———}CH\\ C(N\cdot NHPh)\cdot CH\end{matrix}>C\cdot N_2Ph\cdot$$

I. II.

In favour of formula I is the production of the compound from oxyazobenzene, but against it is the loss of acid properties which are so distinctly characteristic of paroxyazo-compounds. The acetyl derivative, when reduced with zinc-dust and dilute sulphuric acid, yields acetanilide, aniline, and diamidophenol. Hence it behaves, on reduction, like the acetyl derivative of an orthoxyazo-compound, and the author concludes that its constitution is more correctly expressed by formula II.

Phenoldisazotoluene, $OH\cdot C_6H_3(N_2\cdot C_6H_3Me)_2$ [1 : 2 : 4], is obtained by the action of paradiazotoluene chloride on an alkaline solution of paratolueneazophenol. It crystallises from acetic acid in yellowish-brown, nodular aggregates, melts at 170°, and is sparingly soluble in cold alcohol, easily so in benzene and acetic acid. The *acetyl compound* crystallises from alcohol in yellowish-brown plates, melts at 128°, and gives acetoparatoluidide on reduction.

The constitution of phenoldisazo-compounds can be determined as follows:—If a diazo-salt $R'\cdot N:N\cdot Cl$ acts on a paroxyazo-compound $O:C_nH_m:N\cdot NHR$, then a compound of the constitution

$$O:C_nH_{m-1}(N:NR'):N\cdot NHR, \text{ or } O:C_nH_{m-1}(N:NR):(N\cdot NHR'),$$

is formed.

In the first case, a paraquinone derivative; in the second, an orthoquinone derivative is produced. If the disazo-compound is first acetylated and then reduced, in the first case the acetyl compound $Ac\cdot NHR$, and in the second case the compound $Ac\cdot NHR'$, will be obtained. Hence it is possible to distinguish between the para- and ortho-quinone formulæ. For this purpose, the authors have examined the behaviour of phenoldisazoparabenzeneorthotoluene, $OH\cdot C_6H_3(N_2\cdot C_7H_7)\cdot N_2Ph$ [1 : 2 : 4], which is prepared by the action of oxyazobenzene on paradiazotoluene chloride, and has been described by Griess as melting at 110°; the authors, however, find that, when pure, it melts at 121°. The *acetyl compound* crystallises in yellow prisms, and melts at 92°. When reduced in alcoholic solution with zinc-dust and dilute sulphuric acid, it yields acetoparatoluidide, unmixed with acetanilide. Hence the phenoldisazoparabenzeneorthotoluene is an orthoquinone derivative of the formula $CO<\begin{matrix}CH\text{———}CH\\ C(N\cdot NH\cdot C_7H_7)\cdot CH\end{matrix}>C\cdot N_2Ph.$

Phenoldisazo-orthobenzeneparatoluene is obtained by the action of

diazobenzene chloride on an alkaline solution of paratolueneazophenol. It crystallises in brownish-yellow, spherical aggregates, and melts at 115—116°. The *acetyl compound* crystallises from alcohol in transparent, golden prisms, melts at 130°, and yields acetanilide on reduction.

α-Naphtholdisazoparabenzeneorthotoluene.—On mixing an alkaline solution of α-naphtholazobenzene with a solution of paradiazotoluene chloride, a dark-coloured precipitate is obtained from which the disazo-compound cannot be separated by crystallisation. It is obtained pure by hydrolysing the acetyl compound with alcoholic potash, and then forms reddish-brown needles, melts at 165°, and dissolves in concentrated sulphuric acid with a bluish-green coloration. The *acetyl compound*, obtained by the action of acetic anhydride and anhydrous sodium acetate on the crude disazo-compound, is purified by crystallisation from alcohol, and melts at 150°. When reduced, it yields acetoparatoluidide, so that the disazo-compound is an orthoquinone derivative.

Azo-compounds of Resorcinol.—Resorcinoldisazobenzene

$$[(OH)_2 : (N_2Ph)_2 = 1 : 3 : 2 : 4]$$

is obtained by pouring an aqueous solution of diazobenzene chloride (2 mols.) and resorcinol (1 mol.) into a solution of sodium acetate. The product, after recrystallisation from chloroform and alcohol, was converted into the diacetyl derivative (m. p. 137—138°), and the latter reduced with zinc-dust and acetic acid. The products were acetanilide and diamidoresorcinol. Hence the authors express resorcinoldisazobenzene as the disphenylhydrazone of orthodiquinoyl.

Symmetrical resorcinoldisazobenzene, $[(OH)_2 : (N_2Ph)_2 = 1 : 3 : 4 : 6]$, is obtained by pouring a solution of diazobenzene chloride (2 mols.) and resorcinol (1 mol.) into a solution of sodium hydroxide, and precipitating with hydrochloric acid. The diacetyl derivative, on reduction, yields acetanilide.

Parabenzeneazoresorcinol $[(OH)_2 : N_2Ph = 1 : 3 : 4]$ was converted into the diacetyl compound; the latter, on reduction, yields acetanilide and amidoresorcinol.

Acetylbenzeneazoacetone, COMe·CH:N·NPhAc, is prepared according to the method of Japp and Klingemann (Trans., 1888, 525), and melts at 93°. Two preparations, however, gave a compound melting at 65°, which was apparently quite pure. On reduction, both compounds yield acetanilide and a ketine (dimethylaldine, C_6H_8N).

Benzoylbenzeneazoacetone is obtained by boiling a concentrated benzene solution of benzeneazoacetone with benzoic chloride. It crystallises in long, four-sided, colourless prisms, melts at 122°, and is easily soluble in alcohol, ether, benzene, and petroleum. On reduction, it yields benzanilide and a ketine.

Hence the acetyl and benzoyl derivatives of benzeneazoacetone, which is probably a hydrazone, behave on reduction similarly to the analogous derivatives of the orthoxyazo-compounds. E. C. R.

Diazoamido-compounds. By H. Goldschmidt and B. Bardach (*Ber.*, **25**, 1347—1378; see also Abstr., 1891, 1211).—The authors

have continued the cryoscopic experiments described by one of them on the conversion of diazoamido-compounds into amidoazo-compounds, with the view of determining the course of the reaction and to obtain the intermediate compounds formed. If known weights of diazoamidobenzene, paratoluidine, and paratoluidine hydrochloride are employed, then if the freezing point of the solution of the diazoamidobenzene in paratoluidine be determined before adding the hydrochloride, it is possible to calculate the depression of freezing point due to the elimination of 1 or 2 mols. of aniline, so that the reaction can be stopped when either of these points is reached and the products examined. The authors have examined the reaction which takes place between a series of diazoamido-compounds with paratoluidine hydrochloride in paratoluidine solution. The following results were obtained :—

Diazoamidobenzene (3 grams) is dissolved in pure paratoluidine (39·7 grams), and the freezing point of the solution determined with a Beckmann's thermometer, then paratoluidine hydrochloride (2·18 grams, corresponding with 1 mol. of diazoamidobenzene) is added, and the mixture stirred in a bath kept at 50°. At intervals of five minutes, the depression of the freezing point is determined. When the depression corresponding with the evolution of 1 mol. of aniline is reached, the melted mass is poured into water containing sodium hydroxide sufficient to neutralise the hydrochloric acid of the hydrochloride, and the paratoluidine is then brought into solution by the addition of acetic acid. A finely-divided, yellow powder (3·1 grams) is obtained, which, on crystallisation from petroleum, is split into paradiazoamidotoluene (m. p. 115°) and unaltered diazoamidobenzene. Diazoamidobenzenetoluene was not obtained. Other experiments under varying conditions gave similar results ; the diazoamidobenzene being converted into diazoamidotoluene, and this into amidoazotoluene. The first reaction takes place quickly, the second somewhat slowly.

Diazoamido-ψ-cumene crystallises from petroleum in large, yellow plates, and melts at 138° (Noelting and Baumann give the m. p. 130·5, *Ber.*, **18**, 1147). When treated with paratoluidine hydrochloride in paratoluidine solution as described above, it gave paradiazoamidotoluene.

Paradichlorodiazoamidobenzene, when treated in a similar way, gave some amidoazotoluene, and a compound melting at 123°, which is a crystalline mixture of paradiazoamidotoluene and paradichlorodiazoamidobenzene.

Metadichlorodiazoamidobenzene is obtained by the action of metadiazobenzene chloride on metachloraniline suspended in a solution of sodium acetate. On adding petroleum to its solution in benzene, it is precipitated in clusters of pale-yellow, microscopic needles, melts at 107°, and easily soluble in benzene, sparingly so in petroleum. With paratoluidine hydrochloride, it gives a crystalline mixture of metadichlorodiazoamidobenzene and diazoamidotoluene, which melts at 90°.

Mixed diazoamido-compounds which contain the group $C_7H_7{\cdot}NH-$, and those which contain the group $C_7H_7{\cdot}N{:}N-$, are both converted into paradiazoamidotoluene when treated as above with paratoluidine hydrochloride. Thus diazoamidobenzenetoluene, diazoamido-ψ-

cumeneparatoluene, diazoamidoparachlorobenzeneparatoluene, and diazoamidometachlorobenzeneparatoluene all yielded diazoamidotoluene.

Diazoamido-ψ-cumeneparatoluene, $C_6H_4Me{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_2Me_3$, is obtained by the prolonged action of paradiazotoluene chloride on pseudocumidine suspended in a solution of sodium acetate. It crystallises from petroleum in bright yellow, radiating needles, and melts at 106°. The above constitution was proved by the cyanate method (*Ber.*, **21**, 1016 and 2557). With phenyl cyanate, it yields an additive compound, which melts at 102°, and when treated with 10 per cent. sulphuric acid and steamed, gives a compound melting at 211°. The authors, however, were unable to determine if this compound was tolylphenylcarbamide or pseudocumylphenylcarbamide. With paratolyl cyanate, it yields an additive compound which sinters at 120°, melts above 230°, and when mixed with sulphuric acid and distilled in a current of steam, it gives *pseudocumylparatolylcarbamide*. The latter crystallises in colourless needles, and melts at 218°.

Diazoamidoparachlorobenzeneparatoluene, $C_6H_4Me{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_4Cl$, is obtained by the action of paradiazotoluene chloride on parachloraniline suspended in a solution of sodium acetate. It is precipitated by petroleum from benzene in long, radiating needles, and melts at 133°. With phenyl cyanate, it gives an additive compound melting at 122°, and then *parachlorodiphenylcarbamide*. The latter crystallises from alcohol in long, colourless needles, and melts at 237—238°.

Diazoamidometachlorobenzeneparatoluene, $C_6H_4Me{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_4Cl$, is precipitated by petroleum from benzene solution in radiating, lemon-yellow needles, and melts at 103°. With phenyl cyanate, it yields an additive compound melting at 104° with frothing, and then *metachlorodiphenylcarbamide*. The latter crystallises from alcohol in white needles, and melts at 184°.

The authors have also examined the behaviour of diazoamido-compounds towards aniline hydrochloride in aniline solution.

Paradiazoamidotoluene, when treated with aniline hydrochloride in aniline solution, is first converted into diazoamidobenzenetoluene, and finally into tolueneazoaniline.

Diazoamidobenzenetoluene was dissolved in aniline, and treated under varying conditions with aniline hydrochloride. Tolueneazoaniline was obtained, and in no case was diazoamidobenzene formed.

Paradichlorodiazoamidobenzene, by the prolonged action of aniline hydrochloride in aniline solution, is converted into amidoazobenzene. A compound which melts at 118° and crystallises from benzene in yellow needles is also formed, but owing to the small quantity, was not examined.

The conversion of diazoamido-compounds into amidoazo-compounds has been stated to take place as follows:—The diazoamido-compound is converted into free amine and diazochloride, and then the latter unites with the amine to form the amidoazo-compound with evolution of hydrogen chloride. The authors find that this is not the course of the reaction. When diazobenzene chloride is added to pure, dry aniline, it at once yields a dark yellow solution, and on pouring this into dilute soda and examining the product, diazoamidobenzene was

obtained. Amidoazobenzene was not formed. Diazobenzene chloride and paratoluidine also unite directly to form a diazoamido-compound, as, on examining the product, diazoamidobenzenetoluene and diazoamidotoluene were obtained.

It has been shown above that by the action of primary amines on diazoamido-compounds, a new diazoamido-compound is first formed which then yields an amidoazo-compound. It has not been proved at which place in the group –NH·N:N– the split takes place in the formation of the amidoazo-compound. To settle this point tertiary amines have been employed in place of primary amines; for, in this case, the formation of a new diazoamido-compound is not possible. Noelting and Binder have stated that diazoamidobenzenetoluene, when treated with dimethylaniline hydrochloride in a solution of dimethylaniline, yields aniline and paratolueneazodimethylaniline, from which it would seem that the nitrogen chain –NH·N:N– is split at the double bond. The authors find that this is not a general reaction; in many cases the chain splits at the single bond, and in one case it splits partly at the double, partly at the single bond.

Diazobenzene-β-naphthylamine, $PhN{:}N{\cdot}NHC_{10}H_7$, was dissolved in six times the weight of dimethylaniline, the equivalent quantity of dimethylaniline hydrochloride added, and the mixture heated at 60° until a test on boiling with sulphuric acid no longer evolved nitrogen. The mass was then treated with dilute soda and steam distilled. The distillate contained dimethylaniline and aniline, the production of the latter showing that the molecule of the diazoamido-compound is split at the double bond. β-Naphthaleneazodimethylaniline, which ought to be contained in the residue, could not be separated.

Parabromodiazoamidobenzene treated in the same way yielded both parabromaniline and aniline. On account of the resinous properties of the non-volatile residue, the bromodimethylamidoazobenzene could not be isolated. *Parabromodimethylamidoazobenzene* is prepared by the action of parabromodiazobenzene chloride on a dilute alcoholic solution of dimethylaniline in the presence of sodium acetate. It crystallises from alcohol in beautiful, bright-red needles, and melts at 156°.

Metanitrodiazoamidobenzene and paranitrodiazoamidobenzene when treated with dimethylaniline hydrochloride, gave respectively metanitraniline and paranitraniline.

The authors put forward the following as the course of the reaction which takes place in the conversion of diazoamido- into amidoazo-compounds. The molecules of diazoamidobenzene and paratoluidine hydrochloride react together as expressed in the equation

$$NHPh{\cdot}N{:}NPh + C_7H_7{\cdot}NH_2,HCl = C_7H_7{\cdot}NH_2 + N(NHPh)_2Cl.$$

Then in the presence of excess of paratoluidine, aniline is eliminated and the compound $N(NH{\cdot}C_7H_7)_2Cl$ is formed. The latter then gives up its hydrogen chloride to the excess of paratoluidine and changes into diazoamidotoluene. When the diazoamidotoluene predominates, or when the diazoamidobenzene is entirely destroyed, the hydrogen chloride unites with the diazoamidotoluene, and the product $N(NH{\cdot}C_7H_7)_2Cl$ reacts with the excess of toluidine to form $N(NH{\cdot}C_7H_7)_2{\cdot}C_7H_6{\cdot}NH_2$, which then loses toluidine, and is converted

into the amidoazo-compound, $N(NH\cdot C_7H_7)_2\cdot C_7H_6\cdot NH_2 = C_7H_7\cdot NH_2 + C_7H_7\cdot NH\cdot N:C_7H_6:NH$. E. C. R.

Phenylhydrazine Acetate. By H. J. F. de Vries and A. F. Holleman (*Rec. Trav. Chim.*, **10**, 228—230).—Glacial acetic acid (1 mol.) is added to phenylhydrazine (1 mol.) dissolved in a little chloroform. Heat is developed, and white, crystalline plates form, which are separated by the pump and washed with chloroform. The compound melts at 68—69°. It is readily soluble in water, alcohol, ether, and chloroform. It is very unstable, and can only be recrystallised well from chloroform, which, in common with other solvents, causes some decomposition. It becomes brown in 24 hours even in a vacuum. It has an odour of mixed acetic acid and phenylhydrazine. Its aqueous solution reduces Fehling's solution at the ordinary temperature. Its analysis presents some difficulty; the nitrogen may be best determined by acting on the compound with boiling Fehling's solution in Schloesing's apparatus. W. T.

Acid Hydrazides. By F. Bölsing and J. Tafel (*Ber.*, **25**, 1551—1556; compare this vol., p. 710; also Gattermann and others, *ibid.*, 843).—*Isobutyric phenylhydrazide*, $C_4H_7O\cdot N_2H_2Ph$, obtained by heating together phenylhydrazine and isobutyric acid at 150°, and crystallising the product from water, forms colourless leaflets, melts at 140°, and is somewhat sparingly soluble in boiling water, readily so in boiling alcohol. It gives a reddish-brown coloration with concentrated sulphuric acid and potassium dichromate or ferric chloride, and reduces Fehling's solution when gently warmed with it, *Isobutyric diphenylhydrazide*, $C_4H_7O\cdot N_2HPh_2$, is prepared by boiling the last-described compound dissolved in alcohol with copper acetate; it crystallises from alcohol in colourless needles, melts at 171—172°, and distils almost without decomposition; it resembles the corresponding acetyl derivative (*loc. cit.*) in its reactions, and, like this, is without action on Fehling's solution.

Phenylacetic diphenylhydrazide, $CH_2Ph\cdot CO\cdot N_2HPh_2$, is produced by oxidising phenylacetic phenylhydrazide with copper acetate, and forms colourless needles melting at 188°.

Cinnamic diphenylhydrazide, $C_2H_2Ph\cdot CO\cdot N_2HPh_2$, crystallises from a mixture of alcohol and ether in small, faintly-yellow needles, and melts at 205°.

Ethyl oxalate diphenylhydrazide, $N_2HPh_2\cdot CO\cdot COOEt$, crystallises in small needles, melts at 131°, and gives *oxalic acid diphenylhydrazide*, $N_2HPh_2\cdot CO\cdot COOH$, when heated on the water-bath with 5 per cent. aqueous potash; the latter crystallises from dilute acetic acid in microscopic needles, melts at 171°, and, unlike the other acidyl diphenylhydrazines, is readily soluble in ether. When the last compound is heated at 180° in an oil-bath, formic diphenylhydrazide (m. p. 116°), see Gattermann and others (*loc. cit.*) is formed. Acetic diparatolylhydrazide (m. p. 170°), prepared by Gattermann and others (*loc. cit.*), dissolves in concentrated sulphuric acid forming a yellow solution which does not give a blue coloration on the addition of potassium dichromate. Coloured products are obtained when the last com-

pound is treated with alcoholic hydrochloric acid, and on addition of stannous chloride, and distillation of the faintly acidified solution, paraditolylamine passes over.

Acetylparabromophenylhydrazine, $C_8H_9BrN_2O$, prepared by boiling parabromophenylhydrazine with glacial acetic acid, crystallises from alcohol in brownish needles melting at 161°, and gives *acetylparabromodiphenylhydrazine*, $C_{14}H_{12}Br_2N_2O$, on oxidation with copper acetate. It is almost insoluble in hot water and in ether, crystallises from alcohol in delicate, colourless needles, and melts at 214°.

The oxidation of acetyl-α-naphthylhydrazine with copper acetate appears to proceed further than in the above cited cases, and with the exception of a small quantity of naphthalene, no crystalline products were isolated. A. R. L.

Mixed Acid Amides. By A. Pinner (*Ber.*, **25**, 1434—1438).—The author has shown that when acetic anhydride acts on imidoethers, the alkyl group is displaced by acetyl; the compounds obtained have been named imidoacetates, and the constitution OAc·CR:NH assigned to them. The same compounds are formed, to a greater or less extent, according to the conditions, by the action of acetic anhydride on the amidines. On the other hand, propionamidine, when treated with acetic anhydride, yields, as chief product, propionacetamide, $C_3H_5O{\cdot}NHAc$, together with propionamide.

Tafel and Enoch (*Ber.*, **23**, 103) have shown that, by the action of ethyl iodide on the silver compound of benzamide, ethylbenzimidoether, OEt·CPh:NH, is formed, and not ethylbenzamide, COPh·NHEt; that is, benzamide behaves as if it had the tautomeric form OH·CPh:NH. From this result the author is uncertain if the above-mentioned imidoacetates have the constitution OAc·CR:NH or COR·NHAc, and if the mixed acid amides are of the type COR·NH·COR′. He has, therefore, attempted to prepare acetylbenzamide in various ways, but has been successful in only one method. Neither by shaking a solution of acetamide, mixed with sodium hydroxide, with benzoic chloride, nor by the direct action of benzoic chloride on acetamide, can benzoylacetamide or acetylbenzamide be obtained. When acetamide is heated with benzoic chloride, the benzoic chloride acts as a dehydrating agent, and benzoic acid, benzoic anhydride, and acetonitrile, are obtained.

Acetylbenzamide is obtained by boiling benzamide with acetic anhydride for half an hour in a reflux apparatus; benzonitrile and cyanophenin are formed at the same time. The product is made alkaline with potassium carbonate, and the insoluble crystalline mass separated and recrystallised from very dilute alcohol, when the cyanophenin remains undissolved. Acetylbenzamide forms flat, white needles, melts at 120°, and is very easily soluble in alcohol, but only sparingly in water. It is identical with benzimidoacetate, which also melts at 120°, and not at 114°, as formerly stated. Hence, the two isomeric compounds, COPh·NHAc and PhC(NH)·OAc, are not obtained, but one undergoes isomeric change at the moment of formation.

When equivalent quantities of β-naphthamidine hydrochloride and

fused sodium acetate are heated to gentle boiling with 4—5 times the quantity of acetic anhydride for about 15 minutes in a reflux apparatus, the chief product is β-naphthimidine. By prolonging the boiling, less of the imidine is obtained, and naphthamide and naphthoylacetamide are formed. The mixed products are separated as follows:—The cold mixture is diluted with water, and the insoluble portion extracted twice with alcohol, when the imidine remains behind. The alcoholic solution is evaporated, and the residue dissolved in benzene. On cooling the solution, naphthoylacetamide crystallises out, whilst the naphthamide remains in solution.

Naphthimidine, $NH[C(NH)\cdot C_{10}H_7]_2$, crystallises in thick, colourless prisms, melts at 195°, is insoluble in water, very sparingly soluble in hot alcohol and acetic acid, easily in benzene, and is converted into naphthamide by prolonged boiling with acetic acid.

Naphthoylacetamide, $C_{10}H_7\cdot CO\cdot NHAc$, crystallises in large, transparent prisms, melts at 160°, and is sparingly soluble in water, easily in alcohol, very easily in hot benzene, but only sparingly in cold benzene.

Naphthamide crystallises in leaflets, and melts at 191—192°.

E. C. R.

Action of Thiocarbonyl Chloride on Aromatic Thiocarbamides. By M. Freund and H. Wolf (*Ber.*, **25**, 1456—1468).—The products of the action of thiocarbonyl chloride on aromatic thiocarbamides are analogous to those obtained by the action of carbonyl chloride, and investigated by Will (Abstr., 1881, 905).

Thiocarbonylthiocarbanilide, $NPh{:}C<^{S\text{---}}_{NPh}>CS$, is obtained by treating diphenylthiocarbamide, suspended in dry ether, with an ethereal solution of thiocarbonyl chloride. The ether is allowed to evaporate spontaneously, and the residue dried on a porous plate. It crystallises from hot, dilute alcohol, in yellow needles melting at 78—79°. About 15 per cent. of the theoretical yield is obtained. It is very soluble in alcohol, benzene, toluene, and carbon bisulphide, less so in hot acetic acid, chloroform, methyl alcohol, and acetone, and insoluble in water. It dissolves in cold concentrated sulphuric acid, and is precipitated from the solution by water. It becomes slightly brown on exposure to light. When boiled with aniline for an hour, it yields diphenylthiocarbamide. On heating a solution of thiocarbonylthiocarbanilide in absolute alcohol with freshly precipitated mercuric oxide in a reflux apparatus, carbonylthiocarbanilide is obtained. It is not changed when heated with water or dilute hydrochloric acid. On heating with potash (sp. gr. 1·4), it yields aniline, phenylthiocarbimide, hydrogen sulphide, and carbonic anhydride. When heated in a sealed tube with concentrated hydrochloric acid at 100°, no action occurs; at 130°, a little hydrogen sulphide is evolved, and on heating for four hours at 160°, complete decomposition occurs, with formation of hydrogen sulphide and aniline.

When diphenylthiocarbamide, suspended in benzene, is heated on the water-bath with thiocarbonyl chloride, an oil, which readily solidifies, is obtained. The benzene is evaporated, and the mass

extracted with hot absolute alcohol. The residue is sparingly soluble in boiling absolute alcohol, and crystallises from it in needles melting at 156°. It has the composition $C_{14}H_{10}N_2S_3$, and was prepared by Proskauer and Sell (Abstr., 1877, i, 67). The author assigns to it the constitution $\begin{matrix}CS\cdot NPh\\ |\\ NPh\cdot CS\end{matrix}>S$. On treating its alcoholic solution with freshly precipitated mercuric oxide, an oily product was obtained. No reaction occurs on heating with aniline or acetic anhydride. On heating with concentrated potash, phenylthiocarbimide, aniline, hydrogen sulphide, and carbonic anhydride result.

Thiocarbonyldiparatolylthiocarbamide is prepared by the action of an ethereal solution of thiocarbonyl chloride on diparatolylthiocarbamide, suspended in dry ether. The solution is filtered, and the residue washed with ether. By spontaneous evaporation of the ethereal solution, the substance separates in yellow needles melting at 109°. The yield is about 10 per cent. of that required by theory. It is very soluble in hot alcohol, ether, benzene, toluene, carbon bisulphide, and glacial acetic acid, and insoluble in water. When heated with aniline, it probably yields thiocarbanilide and ditolylthiocarbamide. On treatment with mercuric oxide, it gives carbonylditolylthiocarbamide.

Thiocarbonyl-β-dinaphthylthiocarbamide, $C_{22}H_{14}N_2S_2$, is prepared from β-dinaphthylthiocarbamide in a similar manner to the preceding substance. It separates from benzene in yellow, flocculent crystals, and melts at 152° with evolution of gas, leaving a residue which eventually melts at 224°. It is soluble in ether, carbon bisulphide, and hot acetic acid, sparingly so in hot benzene and alcohol.

Carbonylphenylparatolylthiocarbamide, $C_{15}H_{12}N_2SO$, is prepared by the action of carbonyl chloride on phenylparatolylthiocarbamide suspended in toluene. Much hydrogen chloride is evolved, and, on allowing the solvent to evaporate, a crystalline mass is obtained, which separates from dilute alcohol in white needles. It melts at 89° with evolution of carbon oxysulphide, and is soluble in hot alcohol, acetic acid, concentrated sulphuric acid, benzene, carbon bisulphide, and ether. In its preparation, a small proportion of phenylparatolylcarbamide is obtained.

Carbonylphenyl-β-naphthylthiocarbamide, $C_{18}H_{12}N_2SO$, is prepared from phenyl-β-naphthylthiocarbamide in the same manner as the preceding compound. A crystalline mass is obtained, which separates from dilute alcohol in white needles melting at 117°. It is soluble in alcohol, ether, benzene, and acetic acid, and insoluble in water.

Phenyl-β-naphthylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot C_7H_7$, results from the combination of phenylthiocarbimide and β-naphthylamine. It forms white, shining scales, which are soluble in alcohol, ether, carbon bisulphide, and hot acetic acid; it melts at 165°.

W. J. P.

Tertiary Phosphines and Arsines. By O. Holle (*Ber.*, **25**, 1518—1521).—Dimethylphenylphosphine reacts with benzal chloride, yielding a deliquescent substance, the platinochloride of which forms a pale-yellow powder melting at 50°, and has the constitution $(OH\cdot CHPh\cdot PMe_2Ph)_2PtCl_6$. When heated at 100° with benzalde-

hyde and aluminium chloride, it yields the same substance. Diethylphenylphosphine does not react with benzaldehyde.

Dimethylphenylarsine reacts with benzal chloride in the same way as the corresponding phosphine. Diethylphenylarsine does not react with benzal chloride. C. F. B.

Isonitrosoanilacetone. By A. F. Holleman (*Rec. Trav. Chim.*, **10**, 223—227).—Isonitrosoacetone (1 mol.) is dissolved in aniline (1 mol.) diluted with half its volume of alcohol. The reaction takes place with development of heat. The crystalline combination obtained melts with decomposition at 171°. Its formula is $C_9H_{10}N_2O$. It dissolves easily in dilute caustic alkalis with a yellow colour, and is precipitated from the solution by carefully adding mineral acids. Its composition is represented by the formula NPh:CMe·CH:NOH, which accounts for its observed solubility in alkalis. The only other possible formula, COMe·CH:N·NHPh, has been shown by Japp and Klingemann (Trans., 1888, 521) to be that of a substance of very different properties, benzeneazoacetone. Under the name isonitrosoanilacetone, Knorr has described a different substance (Abstr., 1884, 1368), which he has since recognised to be of a nature different from that indicated by the name (*Annalen*, **233**, 82, note).

P. C. Plugge has examined the toxicological properties of this compound. Isonitrosoanilacetone belongs, apparently, to the picrotoxin group of poisons, and acts principally on the spasmodic centres of the brain and medulla oblongata. The convulsions produced differ from those caused by strychnine; reflex tetanus, excited by exterior irritation, does not occur. The poisonous doses for frogs, 0·012—0·015 gram. An injection of 0·008 gram killed a white mouse in three hours. It has no influence on the coagulation of the blood, and does not reduce oxyhæmoglobin or cause the production of methæmoglobin. W. T.

Aromatic Alkyl Ketones and their Oximes. By A. Claus (*J. pr. Chem.* [2], **45**, 377—397; compare Abstr., 1890, 769, 979; 1891, 199, 564, 1222).—In this paper, the author summarises the work on ketones which has lately been done in his laboratory. Most of it has already appeared (*loc. cit.*), and the rules controlling the oxidation of aromatic alkyl ketones have been enunciated (Abstr., 1890, 769). The reduction of these ketones with hydrogen iodide has been the means of isolating a number of hydrocarbons which have as yet only been described in inaugural dissertations, but will be further treated of; they are: *orthethylparisopropyltoluene* (b. p. 204—206°), prepared from paracumyl methyl ketone; *metamethylparethyltoluene* (b. p. 184°), obtained from xylyl methyl ketone; *orthopropylparisopropyltoluene*, *orthobutylparisopropyltoluene*, *orthisobutylparisopropyltoluene*, *orthisoamylparisopropyltoluene*, and *isoamylbenzene*. There are no new compounds definitely described, and the bulk of the paper is occupied by a discussion as to the structure and isomerism of the oximes of these ketones, particularly in reference to Minunni's, Hantzsch's, and Auwers and Meyer's recent dissertations (Abstr., 1891, 1354; this vol., 186, 291, 426, 598). A. G. B.

Oxidation of Cinnamic Acid. By R. Fittig and R. Ruer (*Annalen*, **268**, 27—32; compare this vol., p. 956).—Phenylglyceric acid, $C_9H_{10}O_4$, is formed, together with benzaldehyde, benzoic acid, and oxalic acid, when cinnamic acid is oxidised with potassium permanganate. It crystallises from water in colourless plates, and melts at 141—142° with slight decomposition (compare Lipp, Abstr., 1883, 994), not at about 117° as stated by Anschütz and Kinnicutt (Abstr., 1879, 644); it is not acted on by boiling dilute hydrochloric acid. The barium salt, $(C_9H_9O_4)_2Ba + 2H_2O$, is amorphous, but the calcium salt crystallises in lustrous plates with 4 mols. H_2O, and the silver salt in small needles. F. S. K.

Oxidation of Phenylisocrotonic Acid. By R. Fittig and P. Obermüller (*Annalen*, **268**, 44—50; compare this vol., p. 956).—*Phenylhydroxybutyrolactone*, $O<\begin{matrix}CHPh-\\CO\cdot CH_2\end{matrix}>CH\cdot OH$, prepared by oxidising phenylisocrotonic acid, and boiling the product with dilute hydrochloric acid, crystallises from ether in colourless needles containing $\frac{1}{2}$ mol. H_2O, and loses its water at 100°, or over sulphuric acid; the air-dried lactone melts at 76°. It is readily soluble in hot water, alcohol, and chloroform, but rather sparingly in ether, and almost insoluble in carbon bisulphide; it is not decomposed by boiling water.

Phenyldihydroxybutyric acid, $OH\cdot CHPh\cdot CH(OH)\cdot CH_2\cdot COOH$, is obtained when the lactone is boiled with barium hydroxide and the salt thus formed decomposed with dilute hydrochloric acid; it separates from ether in colourless, monosymmetric crystals, $a : b : c = 1{\cdot}5369 : 1 : 1{\cdot}7226$, $\beta = 79°\ 36'$, melts at 117°, and is readily soluble in alcohol, but rather sparingly in ether, chloroform, carbon bisulphide, light petroleum, and benzene. It dissolves freely in water, and on boiling the solution, especially after adding a few drops of hydrochloric acid, it is converted into phenylhydroxybutyrolactone; the same change takes place when the acid is heated at 100°. The *barium* salt, $(C_{10}H_{11}O_4)_2Ba + H_2O$, crystallises in small, nacreous plates, and is only moderately easily soluble in cold water, and very sparingly in alcohol. The *calcium* salt crystallises in lustrous plates with 1 mol. H_2O. The *silver* salt, $C_{10}H_{11}O_4Ag$, is a colourless, flocculent compound. F. S. K.

Oxidation of Hydrocinnamenylacrylic Acid. By R. Fittig and E. Mayer (*Annalen*, **268**, 50—54; compare this vol., p. 956).—*Phenylhydroxyvalerolactone*, $C_{11}H_{12}O_3$, is produced by the oxidation of hydrocinnamenylacrylic acid. It crystallises from a mixture of chloroform and light petroleum in lustrous, hexagonal plates, melts at 61·5°, and is almost insoluble in light petroleum, very sparingly soluble in cold water, but moderately in hot water, and readily in chloroform and benzene. When the lactone is boiled with bases, it is converted into salts of *phenyldihydroxyvaleric acid;* the acid itself is crystalline, but is very unstable. The *barium* salt, $(C_{11}H_{13}O_4)_2Ba$, crystallises from hot water in lustrous plates, and is rather sparingly soluble in cold water. The *calcium* salt, with 1 mol. H_2O, forms spherical

aggregates, and effloresces in dry air. The *silver* salt, $C_{11}H_{13}O_4Ag$, crystallises from boiling water in small, lustrous needles.

F. S. K.

Decomposition of Phenyldibromobutyric Acid. By R. Fittig, P. Obermüller, and C. Schiffer (*Annalen*, **268**, 71—86; compare this vol., p. 959).—*Phenylbromobutyrolactone*, $\begin{matrix}CO\text{———}O\\ |\\ CH_2{\cdot}CHBr\end{matrix}>CHPh$, is produced when phenyldibromobutyric acid (m. p. 138°) is boiled for a short time with water. It separates from carbon bisulphide in large, monosymmetric crystals, $a : b : c = 0{\cdot}5883 : 1 : 0{\cdot}7897$, $\beta = 64° 44'$, melts at 70°, and is readily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide, but only sparingly in light petroleum or cold water. When boiled with water for about an hour, it is converted into benzoylpropionic acid (m. p. 116°), identical with the compound described by Fittig and Leoni (Abstr., 1890, 895).

When phenyldibromobutyric acid is treated with a slight excess of sodium carbonate, and the solution kept at the ordinary temperature for some time, there are formed phenylbromobutyrolactone (m. p. 70°), phenylisobromobutyrolactone, and phenylisohydroxybutyrolactone, together with yellow or reddish-brown products which could not be obtained in crystals; the relative quantity of these products depends to a considerable extent on the amount of sodium carbonate used and on the duration of the experiment.

Phenylisobromobutyrolactone, $C_{10}H_9BrO_2$, separates from hot carbon bisulphide in lustrous needles, and from the cold solvent in well-defined, transparent, monosymmetric crystals,

$$a : b : c = 1{\cdot}5587 : 1 : 1{\cdot}8056, \beta = 81° 12',$$

melts at 76°, and is gradually converted into benzoylpropionic acid by boiling water.

Phenylisohydroxybutyrolactone, $C_{10}H_{10}O_3$, separates from ether in monosymmetric crystals, $a : b : c = 2{\cdot}2566 : 1 : 3{\cdot}0965$, $\beta = 66° 34'$, melts at 93—94°, and is readily soluble in alcohol, chloroform, and benzene, but only moderately in ether, and very sparingly in cold water; it dissolves slowly in cold sodium carbonate, and separates again unchanged on the addition of hydrochloric acid. *Barium phenylisodihydroxybutyrate*, $(C_{10}H_{11}O_4)_2Ba$, prepared by boiling the isohydroxylactone with barium hydroxide, is a microcrystalline powder, very sparingly soluble in hot water. F. S. K.

Decomposition of Phenyldibromovaleric Acid. By R. Fittig and J. Stern (*Annalen*, **268**, 86—92; compare this vol., p. 959).—*Phenylbromovalerolactone*, $C_{11}H_{11}BrO_2$, prepared by treating phenyldibromovaleric acid with a slight excess of sodium carbonate, at the ordinary temperature, crystallises from ether in prisms, melts at 139—140° with decomposition, and is readily soluble in chloroform, but only sparingly in ether, and very sparingly in light petroleum.

Phenylangelicalactone, $C_{11}H_{10}O_2$, is formed, together with phenyllevulinic acid, when the preceding compound is boiled with water for 5—6 hours; it is a yellowish, mobile oil, having a strong, pepper-

mint-like odour, very readily soluble in ether, but only sparingly in water.

Phenyllevulinic acid, $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, crystallises from a mixture of chloroform and light petroleum in large, lustrous needles, melts at 55—56°, and is readily soluble in ether, benzene, and carbon bisulphide, but only moderately easily in water and sparingly in light petroleum. The *calcium* salt, $(C_{11}H_{11}O_3)_2Ca$, crystallises from water in small needles containing 6 mols. H_2O, and from alcohol in small plates; it loses the whole of its water at 100°. The *barium* salt, with $1\frac{1}{2}$ H_2O, like the calcium salt, is readily soluble in water, and crystallises in small, spherical aggregates; it loses its water at 120°. The *silver* salt, $C_{11}H_{11}O_3Ag$, separates from hot water in plates, and is very stable in the light. When the acid is treated with sodium amalgam in dilute sulphuric acid solution, and the product then boiled with dilute hydrochloric acid, phenylvalerolactone is formed (compare following abstract). F. S. K.

Hydrocinnamenylacrylic Acid. By R. Fittig and J. Stern (*Annalen*, **268**, 92—96).—*Phenyl-γ-bromovaleric acid*,

$$CH_2Ph{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

can be obtained by treating hydrocinnamenylacrylic acid with concentrated hydrobromic acid at the ordinary temperature; it separates from a mixture of chloroform and light petroleum in colourless, prismatic crystals, melts at 58—59°, and is readily soluble in carbon bisulphide, benzene, and chloroform, but only very sparingly in cold light petroleum.

Phenylvalerolactone, $\begin{matrix} CO\text{---}O \\ | \\ CH_2{\cdot}CH_2 \end{matrix}\!>\!CH{\cdot}CH_2Ph$, is formed when the preceding compound is heated with water for a short time, or treated with sodium carbonate at the ordinary temperature; it crystallises from chloroform in thick plates, melts at 33°, and is readily soluble in carbon bisulphide and chloroform, and moderately easily in hot water, but only very sparingly in light petroleum; it has a peppermint-like odour. *Barium phenylhydroxyvalerate*, $(C_{11}H_{13}O_3)_2Ba$, and the corresponding *calcium* salt, obtained by boiling the lactone with barium and calcium hydroxide respectively, are colourless, amorphous powders, soluble in alcohol and water. The *silver* salt separates from hot water in plates.

Phenyl-γ-hydroxyvaleric acid, $C_{11}H_{14}O_3$, is obtained when the calcium salt is decomposed with very dilute hydrochloric acid and the solution immediately extracted with ether; it crystallises from warm water in colourless needles, melts at 101—102° with decomposition, and is readily soluble in carbon bisulphide and chloroform, but only sparingly in light petroleum; when kept for a long time over sulphuric acid, or when warmed with dilute acids, it is converted into the lactone. F. S. K.

New Derivatives of Coumarin. By R. Fittig and R. Claus (*Annalen*, **269**, 1—14; compare this vol., pp. 956, 959).—The authors have attempted, but unsuccessfully, to prepare orthohydroxyphenyl-

propiolic acid in order to compare its properties with those of coumarilic acid, $C_6H_4<\overset{O}{\underset{CH}{>}}C\cdot COOH$ (compare Fittig and Ebert, *Annalen*, **216**, 162), with which it is isomeric.

Ethylcoumarinic acid dibromide (orthethoxyphenyldibromopropionic acid), prepared as described by Fittig and Ebert (*loc. cit.*), melts at 156—162° with decomposition, according as it is slowly or quickly heated, and separates from carbon bisulphide in large, colourless, seemingly rhombic crystals.

Orthethoxy-α-bromocinnamene, $OEt\cdot C_6H_4\cdot CH{:}CHBr$, is formed, together with a small quantity of ethylcoumaric acid and ethoxyphenylacetylene, when ethylcoumarinic acid dibromide is boiled with water for a short time; it is an almost colourless oil of sp. gr. 1·360 at 17°, quickly turns yellow when kept, and boils at 144—147° under a pressure of 15 mm.; it is insoluble in water, but miscible with alcohol, ether, and carbon bisulphide. The *tribromide*, $C_{10}H_{11}OBr_3$, prepared by treating ethoxybromocinnamene with bromine in carbon bisulphide solution, crystallises from alcohol in large, colourless prisms, melts at 51°, and is readily soluble in alcohol, ether, benzene, and carbon bisulphide.

Orthethoxyphenylpropiolic acid, $OEt\cdot C_6H_4\cdot C{:}C\cdot COOH$, can be obtained by boiling orthethoxyphenyldibromopropionic acid with alcoholic potash. It crystallises from water in slender needles, melts at 112—112·5° with decomposition, and is only sparingly soluble in cold, but moderately easily in boiling, water, the hot solution having an intensely irritating odour; it dissolves freely in ether and alcohol. The *calcium* salt, $(C_{11}H_9O_3)_2Ca + 2H_2O$, crystallises from water in colourless prisms, and is only sparingly soluble in cold water; it does not lose its water at 150°, and at 160° it decomposes and turns brown. The *barium* salt, $(C_{11}H_9O_3)_2Ba + 4H_2O$, is a hygroscopic substance, readily soluble in hot alcohol, from which it crystallises in large, colourless prisms; when dried over sulphuric acid, the crystrals effloresce, and then seem to contain 4 mols. H_2O.

Orthethoxyacetophenone, $OEt\cdot C_6H_4Ac$, is produced, together with orthethoxyphenylchloracrylic acid, when ethoxyphenylpropiolic acid is boiled with moderately concentrated (1 : 1) hydrochloric acid; it crystallises from boiling water in thin, broad prisms, melts at 38·5—39·5°, is volatile with steam, and is readily soluble in alcohol and ether, but only very sparingly in water.

Orthethoxyphenylchloracrylic acid, $OEt\cdot C_6H_4\cdot CCl{:}CH\cdot COOH$, crystallises from water, in which it is moderately easily soluble, in small, colourless needles melting at 108—109°; it is slowly decomposed by boiling dilute hydrochloric acid, being converted into ethoxyacetophenone, and, on reduction with sodium amalgam, it yields orthethoxyphenylpropionic acid (m. p. 80—81°).

Ethoxyphenylacetylene, $OEt\cdot C_6H_4\cdot C{:}CH$, is formed when sodium ethoxyphenylchloracrylate is boiled with water, and when ethoxyphenylpropiolic acid is heated with water at 140—150°; it is also produced in small quantities in the preparation of ethoxybromocinnamene in the manner described above. It is a colourless oil, and gives with an alcoholic ammoniacal solution of silver nitrate a colour-

less, crystalline compound of the composition $C_{10}H_9OAg$, which is stable in the light. F. S. K.

Ellagic Acid. By G. Goldschmiedt and R. Jahoda (*Monatsh.*, **13**, 49—57).—Zölffel (Abstr., 1891, 918) and Schiff state that this acid gives a tetracetyl derivative, when digested with acetic anhydride, whilst Barth and Goldschmiedt (*Ber.*, **11**, 846) describe the product as a pentacetyl derivative. In order to determine which of these statements is correct, the authors have prepared the acetyl compound, and submitted it to analysis by three different methods, including those used by the investigators named above; the results, however, obtained by those processes give widely varying numbers. When heated with a large excess of benzoic chloride, ellagic acid gives a well-characterised benzoyl derivative, which forms a yellowish-white, crystalline powder, contains four benzoyl groups, and is unchanged when again heated with benzoic chloride at 295—300°. It follows, therefore, that ellagic acid contains only four hydroxyl groups. G. T. M.

Ethylpseudocumene and the Action of Sulphuric Acid on it. By A. Töhl and D. v. Karchowski (*Ber.*, **25**, 1530—1533).—*Ethylpseudocumene*, $C_6H_2Me_3Et$ [$Me_3 : Et = 1 : 2 : 4 : 5$], was prepared by treating the bromopseudocumene, melting at 72—73° with ethyl bromide and sodium. It boils at 206—208°, and a further proof of its constitution is that, when oxidised with dilute nitric acid, it yields durylic acid, melting at 148°. When treated with excess of bromine in the presence of iodine, it yields *dibromethylpseudocumene*, which crystallises from alcohol, in which it is sparingly soluble, in needles melting at 218°.

When treated with strong sulphuric acid, much remains unaltered, but an *ethyltrimethylbenzenesulphonic acid* is formed, whose *barium salt*, $(C_{11}H_{15}\cdot SO_3)_2Ba$, crystallises with 1 mol. H_2O, and whose *sulphonamide* melts at 153°. This sulphonic acid is probably derived from the original hydrocarbon, for, when its sodium salt is heated at 180° with strong hydrochloric acid, a hydrocarbon is obtained, which boils at 206—209°, and yields a dibromo-derivative melting at 217—218°, showing that it is ethylpseudocumene. When ethylpseudocumene is treated with chlorosulphonic acid, another *ethyltrimethylbenzenesulphonic acid* is formed, whose *potassium*, $C_{11}H_{15}\cdot SO_3K$, and *barium* $(C_{11}H_{15}\cdot SO_3)_2Ba$, *salts* crystallise with 1 and 3 mols. H_2O respectively, and whose *sulphonamide* melts at 86°. It is, therefore, not identical with the above-mentioned isomeric sulphonic acid, but is probably the second sulphonic acid theoretically obtainable from ethylpseudocumene.

Sulphuric acid thus causes no shifting of the side groups of ethyl pseudocumene (as it does in the case of durene; compare this vol., p. 968), but only forms an ethylpseudocumenesulphonic acid. C. F. B.

Aromatic Thiosulphonates. By R. Otto and E. Heydecke (*Ber.*, **25**, 1477—1483).—*Ethylene paratoluenethiosulphonate*, $(C_7H_7\cdot SO_2S)_2C_2H_4$,

is prepared by heating ethylene bromide with potassium paratoluenethiosulphonate in molecular proportion, in alcoholic solution, in a reflux apparatus; it is readily soluble in benzene or ether, and crystallises from alcohol in colourless plates which melt at 76—77°, and probably belong to the monosymmetric system; on heating with potash, the compound yields potassium ethylenedisulphinate, potassium toluenesulphinate, and diethylene tetrasulphide, the formation of the latter compound being preceded by that of ethylene mercaptan. On heating the ethereal salt with potassium sulphide, diethylene tetrasulphide, ethylene mercaptan, and potassium toluenethiosulphonate are formed; whilst with zinc and hydrochloric acid in alcoholic solution, ethylene mercaptan, toluenesulphinic acid, and toluene hydrogen sulphide are produced. By the action of zinc dust and alcohol at 150° on the ethereal salt, the zinc compounds of ethylene mercaptan and toluenesulphinic acid are obtained.

Ethylene benzenethiosulphonate crystallises, in all probability, in the monosymmetric system; by the action of bromine in aqueous or alcoholic solution, ethylenedisulphonic acid and benzenesulphonic acid, together with a little sulphuric acid, are formed. J. B. T.

Products from Indigo-blue. By C. O'Neill (*Chem. News*, **65**, 124).—When pure indigo-blue is treated with 20—30 times its weight of glacial acetic acid and gradually with about $\frac{1}{4}$ its weight of permanganate or a corresponding quantity of lead or manganese peroxide, the mass thickens, the blue disappears, and by filtering, washing, and drying in a vacuum, or at 20—25° in the air, a crystalline substance is obtained in quantities amounting to 140 per cent. of the indigo used; this the author terms "*oxyacetoindigotin*." This compound is insoluble in all solvents; is permanent in dry air and, in the cold, in most neutral, acid, and oxidising agents, but is attacked by alkalis and decomposed by heat, yielding, in the presence of moisture, acetic acid, isatin, indigo, and an oxidised product, crystallising from chloroform in silky, golden-yellow crystals, slightly soluble in water, and, unlike isatin, soluble in carbon bisulphide. In dry heat, oxyacetoindigotin loses 31—32 per cent. of its weight, and is resolved into glacial acetic acid, indigo, and a resinous substance soluble in chloroform. With sodium hydroxide in the cold, oxyacetoindigotin yields indigo, sodium acetate, and a salt of an acid, indigotic acid, $C_{32}H_{28}N_4O_{12}$, which separates from alcohol in brilliant crystals; it can also be crystallised from hot water, although 1000 parts of cold water are required for its solution. It decomposes at 240°, yielding, among other products, aniline. It is polybasic, and, of two sodium salts, $C_{32}H_{26}Na_2N_4O_{12}$ and $C_{32}H_{27}NaN_4O_{12}$, the former is very soluble and not crystalline, the latter is less soluble and crystallises well from water. When heated with glacial acetic acid, oxyacetoindigotin is decomposed into acetic acid, indigo, and brilliant, yellow crystals, containing a new substance of the composition C_8H_3NO. D. A. L.

Indigo-green. By V. H. Soxhlet (*Chem. Zeit.*, **15**, 913—914).—The author, some time ago, was engaged in the commercial testing of some indigo-carmines, when, by accident, some indigo solution

got mixed with a considerable quantity of ammonia. Fortunately, this mixture was not thrown away, but corked up and put aside: after the interval of a fortnight, it was noticed that the colour was not, as might have been expected, a dark blue, but had changed to a yellowish-green.

It was evident that the liquid contained several colouring matters, and this was confirmed by the simple, well-known device of dropping some of it on blotting-paper. On consulting the literature on the subject, the author came to the conclusion that the only substance which bears a certain resemblance to the compound is Berzelius' viridinesulphonate; this, although a green colouring matter, is only soluble in absolute alcohol, and has, as yet, found no technical application.

The author now weighed off equal portions of indigocarmine and put them into bottles containing increasing quantities of ammonia, where they were allowed to remain for about 10 days. It now appeared that those portions which contained the largest quantity of ammonia had the purest green tinge, whilst the others had still a good deal of blue shade about them. It was not to be expected that the green colouring matter in its alkaline state would be able to dye wool, and this was confirmed by an experiment on the small scale. A portion of the solution was now faintly acidified with dilute sulphuric acid and then mixed with brine of 1·1 sp. gr. The filtrate was pale green, with a reddish reflex, not at all unlike Berzelius' viridinesulphonic acid. The paste obtained resembles commercial indigocarmine in appearance, without, however, showing the coppery lustre. In warm water it is readily soluble, and woollen threads immersed in the hot solution look as if they have been dyed with methyl-green and show well by artificial light. The dying process proceeds very regularly, in fact better than with the indigo preparations. The goods, moreover, resist the action of alkalis and soap better, although experiments in this direction must still be carried out on the large scale.

In trying to prepare large quantities of indigo-green, the author used the dry commercial indigo extract such as is manufactured and used in England. This is easier to mix with the ammonia than the pasty product, and it also contains less free acid.

The prolonged action of ammonia does not yield a superior product, but rather the reverse. The author thinks that his indigo-green is composed of at least two colouring matters, a yellow and a green dye. L. DE K.

Formation of Closed Chain Compounds by the Elimination of Bromine from the Benzene Nucleus. By W. R. CATHCART, Jun., and V. MEYER (*Ber.*, **25**, 1498—1500).—*Orthobromobenzophenone*, C_6H_4BrBz, prepared by the mutual action of orthobromobenzoic chloride, benzene, and aluminium chloride, melts at 42°; by the action of hydroxylamine hydrochloride, the corresponding hydroxime is formed, but with hydroxylamine in alkaline solution an isoxazole derivative is obtained which readily crystallises, melts at 83—84°, and in small quantities may be distilled without decomposi-

tion; it does not combine with alkalis. The compound has the formula $C_6H_4<\begin{matrix}O\cdot N\\ \|\\ -C\,Ph\end{matrix}$, and on account of its relation to indene the authors propose to term the complex $C_6H_4<\begin{matrix}O\\ C\end{matrix}>N$, *indoxazene*.

The hydroximes of the following symmetrical compounds only exist in one form, meta- and para-dibromo-, paradichloro-, paradiiodo-, paradimethyl-, and paradimethoxy-benzophone. J. B. T.

Synthesis of Symmetrical Triphenylbenzene. By M. Delacre (*Bull. Acad. roy. Belg.* [3], **22**, 470—502).—*Dypnopinacone*, $C_{32}H_{28}O_2$, is obtained by heating a mixture of zinc ethyl and dypnone, $CMePh{:}CH{\cdot}COPh$, dissolved in anhydrous ether, but it is most conveniently prepared by gently heating on the water-bath in a reflux apparatus a mixture of zinc ethyl (20 grams), acetophenone (30 grams), and anhydrous ether (200 grams). If the operation is conducted too vigorously, α-dypnopinacolin is obtained. As soon as effervescence commences, the source of heat is removed, and the heating only resumed after some hours. At the end of two or three days, the mixture no longer fumes; the ether is then distilled off, the residue heated at the full temperature of the water-bath for some time, recohobated with ether, and the residue, after distilling off the latter, treated with dilute acid and crystallised from alcohol (500 c.c.); the compound forms white needles, melts at 160·5—161°, and is sparingly soluble in ether and cold alcohol, more readily so in benzene. When the alcohol is distilled from the mother liquor, two isomeric dypnopinacolins and an organo-zinc compound melting at 118°, which is being investigated, may be isolated. The alcoholic character of dypnopinacone is little pronounced, and attempts to prepare an acetyl derivative were unsuccessful; alcoholic potash converts it into an acid and a hydrocarbon of the type of triphenylmethane; when heated with glacial acetic acid, an intensely yellow solution results, from which α-dypnopinacolin separates on cooling; the same compound is obtained by the action of acetic anhydride, acetic chloride, and phosphorus trichloride; in the two last cases, however, "ψ-dypnopinacolin" is also produced; phosphorus pentachloride gives α-dypnopinacolin and dehydrodypnopinacolin; whilst, on fusion or by treatment with zinc ethyl, it yields α-dypnopinacolin, and an isomeride (m. p. 177°). When dypnopinacone is distilled under a pressure of 15 mm., a mixture of acetophenone, dypnone, a crystalline hydrocarbon (m. p. 106—107°), and water pass over below 250°, whilst symmetrical triphenylbenzene remains. Dypnopinacone has probably the constitution

$$\begin{matrix}CH_2{\cdot}CPh{:}CH{\cdot}CPh{\cdot}OH\\ |\qquad\qquad\qquad\quad|\\ CH_2{\cdot}CPh{:}CH{\cdot}CPh{\cdot}OH\end{matrix}$$

α-Dypnopinacolin, $C_{32}H_{26}O$, is obtained, as already stated, by treating dypnopinacone with glacial acetic acid, but to avoid the production of a trace of the isomeride (m. p. 177°), it is advisable to heat cautiously. It forms brilliant sulphur-yellow crystals, melts at

133·5—134°, and is readily soluble in hot glacial acetic acid, sparingly so in the cold liquid, alcohol, and ether. When heated on the water-bath with phosphorus trichloride, or in a closed vessel at 100° with dilute hydrochloric acid, or when a current of hydrogen chloride is passed through the fused substance, β-dypnopinacolin (m. p. 140·5—141°) is produced. The same compound is obtained by heating the α-derivative in a sealed tube at 150—180°, as also by boiling it with 10 per cent. alcoholic potash; it does not react with alcoholic hydroxylamine. When equal weights of α-dypnopinacolin, dissolved in benzene, and phosphorus pentachloride are heated together on the water-bath for several hours, dehydrodypnopinacolin (see below) is obtained. The α-modification is instantly converted into the β-derivative when its solutions are heated with mineral acids; whilst by heating them with nitric acid oxidation derivatives of the β-compound are obtained. When α-dypnopinacolin is distilled under diminished pressure, it decomposes into symmetrical triphenylbenzene and acetophenone. The author suggests the following constitution for α-dypnopinacolin, $\begin{matrix}CH_2\cdot CPh{:}CH\\ CH_2\cdot CPh{:}CH\end{matrix}>CPh\cdot COPh$. The argument used in support of the symmetrical constitution of β-benzopinacolin (Abstr., 1891, 456) applies also in the case of α-dypnopinacolin.

α-Dypnopinacolin alcohol, $\begin{matrix}CH_2\cdot CPh{:}CH\cdot CPh\cdot OH\\ CH_2\cdot CPh{:}CH\cdot CHPh\end{matrix}$, is prepared by heating a mixture of dypnopinacolin (4·6 grams) and zinc ethyl (11 grams) on the water-bath for four days; ethylene passes off during the reaction, and the product is treated with dilute acid, and crystallised from alcohol, when it is obtained in large, white crystals, and melts at 138·5—139°. It reacts with acetic chloride forming *dypnopinacolene*, $\begin{matrix}CH_2\cdot CPh{:}CH\cdot CPh\\ CH_2\cdot CPh{:}CH\cdot CPh\end{matrix}$. The latter is obtained when a mixture of dypnone (40 grams) and zinc ethyl (20 grams) is heated on the water-bath for three days; it crystallises from alcohol in white, nacreous scales, melts at 95·5—96°, and, when distilled at the ordinary pressure, decomposes into symmetrical triphenylbenzene and phenylethylene.

β-Dypnopinacolin, $\begin{matrix}CH_2\cdot CPh{:}CH\cdot CPh\\ CH_2\cdot CPh{:}CH\cdot CPh\end{matrix}>O$, is prepared from the α-derivative as above described; it separates from alcohol or acetic acid in well-formed crystals, melts at 140·5—141°, does not react with phenylhydrazine or hydroxylamine, and only reacts with zinc ethyl when heated at 180—200°, giving rise to oily products. When it is distilled under diminished pressure, it decomposes into the same products as the α-derivative, and, on heating it for three hours in a reflux apparatus with alcoholic potash at 180°, it decomposes into benzoic acid and a hydrocarbon, $\begin{matrix}CH_2\cdot CPh{:}CH\\ CH_2\cdot CPh{:}CH\end{matrix}>CHPh$, melting at 95·5°; whilst on heating it in a sealed tube with a large excess of alcoholic potash at 200—210°, a hydrocarbon is produced which crystallises from alcohol in prisms, melts at 145°, and probably has the constitution $CHPh(CH{:}CMePh)_2$.

Dehydrodypnopinacoline, $C_{32}H_{24}O$, is obtained when a few drops of nitric acid are added to a solution of β-dypnopinacolin in glacial acetic acid; it crystallises from alcohol in white, satiny tufts, melts at 186·5—187°, distils under diminished pressure at a very high temperature without decomposition, does not react with phenylhydrazine or hydroxylamine, and resists the action of those reagents which attack the dypnopinacolins. It gives dypnopinacolene (see above) when heated with hydriodic acid at 200°, and its constitution is represented by one of the following formulæ, $\begin{matrix}CH\cdot CPh{:}CH\cdot CPh\\ \|\quad\quad\quad\quad|\\ CH\cdot CPh{:}CH\cdot CPh\end{matrix}>O$ or $\begin{matrix}CH_2\cdot CPh{:}C\cdot CPh\\ |\quad\quad\quad\quad|\\ CH_2\cdot CPh{:}C\cdot CPh\end{matrix}>O$. Further experiments are in progress.

A. R. L.

Action of Phenylhydrazine on Unsaturated γ-Diketones. By F. Klingemann (*Annalen*, **269**, 104—130).—The author has studied the action of phenylhydrazine on Zinin's "acicular oxylepidene," a compound which has been shown by Magnanini and Angeli (Abstr., 1889, 729) to be $\alpha\beta$-dibenzoylstilbene, CPhBz:CPhBz; the action of phenylhydrazine on $\alpha\beta$-dibenzoylcinnamene has been previously investigated by Japp and Huntly (Trans., 1888, 184) and by Japp and the author (Trans., 1890, 671).

Two compounds are formed when dibenzoylstilbene is heated at 100° with an equal weight of phenylhydrazine in alcoholic solution; on boiling the brown, oily product with alcohol, a lemon-yellow powder of the composition $C_{31}H_{26}N_2$ is precipitated, and the filtered solution, on evaporation, yields an orange, crystalline compound of the composition $C_{34}H_{28}N_2O$, which melts at 201° with decomposition, and dissolves in concentrated sulphuric acid with a reddish-brown coloration. The yellow powder is in all probability *anilidotetraphenylpyrroline*, $\begin{matrix}CPh{:}CPh\\ |\quad\quad|\\ CPh{:}CPh\end{matrix}>N\cdot NHPh$; it separates from alcohol in microscopic crystals, melts at 207°, and dissolves in concentrated sulphuric acid with a green coloration; when submitted to dry distillation, it yields three compounds, one of which only was analysed, and found to be a tetraphenylpyrroline (m. p. 206—207°), identical with the compound described by Garrett (Abstr., 1889, 162) and by Fehrlin (Abstr., 1889, 623).

At least two compounds are formed when a glacial acetic acid solution of phenylhydrazine is gradually added to a boiling glacial acetic acid solution of dibenzoylstilbene, and the mixture boiled for 10 minutes; on neutralising the cold diluted acetic acid solution with soda, a precipitate is produced which is partially soluble in boiling alcohol. The insoluble, almost colourless residue does not melt at 340°, and is insoluble in all ordinary solvents except acetic acid, with which it seems to form a salt; its composition may be approximately represented by the formula $C_{12}H_9NO$, but it is possibly a mixture. The reddish-brown alcoholic solution contains a compound of the composition $C_{27}H_{22}N_2$; this substance crystallises from ethyl acetate, in which it is moderately easily soluble, in small four-sided, yellowish-brown plates, melts at 212—213°, and is probably a

dihydrotetraphenylpyrazole. When the acetic acid solution referred to above is neutralised with ammonia instead of with soda, neither of the compounds just described is precipitated, but in their place a yellow substance of the composition $C_{34}H_{28}N_2O$ is obtained; this compound separates from a mixture of ethyl acetate and light petroleum in yellow needles, melts at 196° with decomposition, and gives no coloration with concentrated sulphuric acid.

$\alpha\beta$-Dibenzoylcinnamene and phenylhydrazine interact in boiling acetic acid solution yielding a yellow, amorphous powder of the composition $C_{36}H_{30}N_4O$, melting at 110—120° with decomposition, and a compound of the composition $C_{28}H_{22}N_2$, identical with the substance previously described by Japp and Huntly (*loc. cit.*).

The bidesyls do not react with phenylhydrazine in alcoholic or in glacial acetic acid solution; diphenyldinitrosacyl and its isomeride (compare Hollemann, Abstr., 1888, 275; 1889, 49) are both readily decomposed by phenylhydrazine yielding the hydrazide of benzoic acid. F. S. K.

Amidonaphtholsulphonic Acids. By F. Reverdin and C. de la Harpe (*Ber.*, **25**, 1400—1409).—By warming amidonaphtholsulphonic acid [OH : NH_2 : SO_3H = 1 : 2 : 4], dissolved in sodium carbonate, on the water-bath in the presence of air, a violet dye is obtained which dyes wool black in an acid bath, and is very stable towards soap and light. A dye having the same properties is obtained by sulphonating the oxidation product of amidonaphthol described by Liebermann under the name imidoxynaphthalene. The authors have examined a series of amidonaphtholsulphonic acids, and determined the nature of the dyes formed from each.

Of α-naphthol derivatives, only those which contain the hydroxyl group in the ortho-position to the amido-group give violet-black dyes similar to that obtained from the 1 : 2 : 4-amidonaphtholsulphonic acid. Those sulphonic acids which contain hydroxyl in the para-position to the amido-group yield brown dyes which are of no value.

Of β-naphthol derivatives, those which contain the hydroxyl group in the ortho-position to the amido-group yield dyes which dye wool in an acid bath a reddish-brown shade, and dye cotton mordanted with metallic bases grey to greyish-green. The amidonaphtholsulphonic acid [OH : NH_2 : SO_3H = 2 : 1 : 5] yields a dye which imparts a yellowish-brown shade to wool, and is not fixed by metallic mordants. The disulphonic acid [NH_2 : OH : SO_3H : SO_3H = 1 : 2 : 3 : 3′] yields no dye. The disulphonic acid

$$[NH_2 : OH : SO_3H : SO_3H = 1 : 2 : 1' : 2']$$

yields a small quantity of a dye which dyes wool a dirty reddish-violet shade. E. C. R.

Pinylamine. By O. Wallach and G. Lorentz (*Annalen*, **268**, 197—210; compare Abstr., 1890, 1316; 1891, 1078).—Pinylamine, when freshly prepared, is a thick, colourless oil, but, unless kept in sealed vessels, it soon turns yellow, and decomposes with liberation of ammonia; its sp. gr. is 0·943 at 17°, and it dissolves freely in

alcohol, ether, and chloroform, but is almost insoluble in water. The *hydrochloride*, $C_{10}H_{15}\cdot NH_2,HCl$, crystallises from water in needles, melts at 229—230° with decomposition, and is very readily soluble in water and alcohol, but insoluble in ether. The *platinochloride*, $(C_{10}H_{15}\cdot NH_2)_2,H_2PtCl_6$, forms yellow plates or needles, and decomposes when heated above 200°, but without melting; it dissolves freely in alcohol, but is only sparingly soluble in water. The *nitrate*, $C_{10}H_{15}\cdot NH_2,HNO_3$, crystallises from dilute alcohol in long, colourless needles, and is very sparingly soluble in cold water, but more readily in alcohol. The *sulphate*, $(C_{10}H_{15}\cdot NH_2)_2,H_2SO_4$, forms small needles, and decomposes at a temperature above 200°, but without melting. The *thiocyanate*, $C_{10}H_{15}\cdot NH_2,HCNS$, separates from water in well-defined, colourless prisms, melts at 135—136°, and is readily soluble in alcohol and ether, but more sparingly in water. The *oxalate*, $(C_{10}H_{15}\cdot NH_2)_2,H_2C_2O_4$, melts at 247—248° with decomposition, and is only very sparingly soluble in almost all ordinary solvents. The *picrate* crystallises in small, yellow needles, and dissolves freely in hot water, alcohol, and ether. The *acetyl* derivative, $C_{10}H_{15}\cdot NHAc$, separates from hot light petroleum and from alcohol in colourless crystals which melt at 108—109°, and are insoluble in water. The *benzoyl* derivative, $C_{10}H_{15}\cdot NHBz$, crystallises from hot light petroleum and glacial acetic acid in small, colourless needles melting at 125°.

Pinylcarbamide, $C_{10}H_{15}\cdot NH\cdot CO\cdot NH_2$, prepared by treating pinylamine hydrochloride with potassium cyanate in aqueous solution, crystallises in long, colourless needles, melts at 156°, and is almost insoluble in water and ether, but readily soluble in alcohol.

Benzylidenepinylamine, $C_{10}H_{15}\cdot N{:}CHPh$, the condensation product of the amine and benzaldehyde, separates from alcohol in crystals, melts at 52—53°, and decomposes on keeping.

Furfuropinylamine, $C_{10}H_{15}\cdot N{:}CH\cdot C_4H_3O$, separates from alcohol in crystals melting at 80—81°.

Parahydroxybenzylidenepinylamine, $C_{10}H_{15}\cdot N{:}CH\cdot C_6H_4\cdot OH$, obtained from pinylamine and salicylaldehyde, forms lustrous, yellow crystals, and melts at 108—109°.

When anhydrous pinylamine hydrochloride is submitted to dry distillation, it is decomposed into ammonium chloride, cymene, and a small quantity of a compound boiling at 200—208°, which has the composition $C_{10}H_{16}O$, and from which a crystalline oxime, $C_{10}H_{16}\cdot NOH$, melting at 87—88°, can be obtained. F. S. K.

Constitution of Pinene. By O. Wallach (*Annalen*, **268**, 210—216).—The author replies to the criticisms of Wagner (Abstr., 1891, 1242), and maintains that the formula which Wagner assigns to pinene does not explain the reactions of the compound as well as that previously put forward by the author (Abstr., 1891, 1081); nevertheless, the latter is to be regarded simply as the best representation which can at present be given, and not as a final expression of the truth. F. S. K.

Nitrolamines of Pinene. By O. Wallach and E. Früstück (*Annalen*, **268**, 216—225).—Primary fatty amines interact readily

with pinene nitrosochloride in moderately concentrated warm alcoholic solution, and on pouring the mixture into water, the nitrolamine is precipitated as an oil, which solidifies after some time, and can then be recrystallised from dilute alcohol; the following compounds were prepared in this way:—

Pinenenitrolpropylamine, $NHPr{\cdot}C_{10}H_{16}{\cdot}NO$, separates from dilute alcohol in colourless crystals melting at 96°.

Pinenenitrolamylamine, $C_5H_{11}{\cdot}NH{\cdot}C_{10}H_{16}{\cdot}NO$, crystallises in colourless plates, and melts at 105—106°.

Pinenenitrolallylamine, $C_3H_5{\cdot}NH{\cdot}C_{10}H_{16}{\cdot}NO$, separates from 90 per cent. alcohol in crystals which melt at 94°, and contain 1 mol. C_2H_6O. When treated with a molecular proportion of bromine in sulphuric acid solution, it yields a crystalline compound melting at 138—139°, which has the composition $C_3H_5Br{\cdot}NH{\cdot}C_{10}H_{16}{\cdot}NO$; when hydrogen bromide is passed into a dry, ethereal solution of the nitrolamine, the *hydrobromide* is deposited in colourless needles melting at 147°, and readily soluble in water; on treating the nitrolamine with bromine in well-cooled glacial acetic acid solution, there is formed a colourless, crystalline compound which melts at 163—164°, and has the composition $C_3H_5Br_2{\cdot}NH{\cdot}C_{10}H_{16}{\cdot}NO,HBr$.

When pinenenitrolbenzylamine is heated at 160—180° in a stream of hydrogen, benzylamine distils, and there remains a solid substance, which is almost insoluble in the usual solvents, and which melts only at a temperature above 300°; this solid product has the composition $C_{10}H_{15}NO$, and is probably a polymeride of nitrosopinene, identical with the compound obtained by Tilden (Trans., 1875, 517), by heating nitrosopinene with benzene or oil of turpentine at 180°. Pinenenitrolallylamine undergoes a similar decomposition at 150—160°.

F. S. K.

Preparation of Pinole Glycol and its Derivatives. By O. Wallach and E. Früstück (*Annalen*, **268**, 222—225).—Pinole glycol diacetate (Abstr., 1891, 217) can be easily obtained by heating pinole dibromide with lead acetate in glacial acetic acid solution at 150°; pinole glycol can be prepared directly from the bromide by boiling the latter with freshly precipitated lead hydroxide and water for several hours, and then extracting the filtered solution with chloroform.

Pinole glycol dipropionate, $(C_2H_5{\cdot}COO)_2C_{10}H_{16}O$, prepared by heating a propionic acid solution of the dibromide with silver propionate, or by warming the glycol with propionic anhydride, melts at 106°, and is insoluble in water.

When pinole dibromide is heated at 100° for three hours with formic acid, it is converted into pinene.

F. S. K.

Tetrahydropinene. By O. Wallach and A. Berkenheim (*Annalen*, **268**, 225—228).—*Tetrahydropinene*, $C_{10}H_{20}$, is formed when hydrochloropinene is reduced with hydriodic acid and amorphous phosphorus at 200°; it boils at 162°, has a sp. gr. of 0·795 at 20°, and its refractive energy is $n_D = 1{\cdot}43701$ at 20°. It is not acted on by a mixture of concentrated nitric acid and sulphuric acid in the cold,

but it is readily oxidised by hot nitric acid yielding oily products; when it is kept in contact with bromine, evolution of hydrogen bromide soon sets in. On prolonged shaking with a warm solution of potassium permanganate, the hydrocarbon is oxidised to carbonic anhydride, oxalic acid, and an acid which, from its smell and an analysis of its silver salt, was thought to be valeric acid. Tetrahydropinene is probably hexahydrocymene, and is doubtless identical with the hydrocarbon obtained by Orlow (*Ber.*, **16**, 799) by the reduction of oil of turpentine. F. S. K.

Nitroketone from Camphosulphophenols. By P. Cazeneuve (*Compt. rend.*, **114**, 838—840). — Amethylcamphophenolsulphone, $C_9H_{12}(SO_2)(OH)_2O$, and amethylcamphophenolsulphonic acid,

$$C_9H_{12}(SO_2{\cdot}OH)(OH)O,$$

when treated with nitric acid, both lose the whole of their sulphur in the form of sulphuric acid, and yield a nitroketone of the composition $C_9H_{11}(NO_2)O$. 10 grams of amethylcamphophenolsulphone is dissolved in 300 grams of hot water, mixed gradually with 20 grams of ordinary nitric acid, and allowed to cool. If the liquid is allowed to boil, the product is decomposed. When the operation is successful, no gas is evolved, and the nitroketone gradually separates as a yellowish oil, which afterwards solidifies. It crystallises from alcohol in golden-yellow needles which melt at 47—48°, sublimes without alteration when heated in small quantity, boils at 260—262° with partial decomposition when heated in large masses, and is volatile in steam. It is only slightly soluble in boiling water, from which it separates in brilliant plates, but is soluble in alcohol, ether, benzene, and other hydrocarbons. It is optically inactive.

The energy of the acid function is comparable with that of carbonic acid. The potassium and ammonium salts crystallise from water, the former in red crystals resembling those of potassium platinocyanide. The calcium, barium, and copper salts are insoluble in water, but soluble in alcohol. The lead, silver, and ferric salts are likewise insoluble, and are prepared by double decomposition. Most of the alkaloïds form resinous, yellow precipitates with a solution of one of the alkaline salts.

Acetic anhydride has no action on the ketone; hydroxylamine yields no oxime, but phenylhydrazine forms a liquid azone. Acetic chloride acts violently on the alkaline salts, and seems to form an acetyl derivative; tin and hydrochloric acid yield a base.

The nitroketone dyes silk yellow without a mordant.

C. H. B.

Action of Phenylhydrazine on Cantharidin. By L. Spiegel (*Ber.*, **25**, 1468—1470).—In the preparation of cantharidinphenylhydrazone (Abstr., 1890, 640), a small proportion of a substance of the composition $C_{16}H_{20}N_2O_4$ is obtained. This compound melts at 194—195°, and is very stable towards chemical reagents, long heating with concentrated hydrochloric acid having no effect on it. By heating it at 110°, it gradually loses weight, until its composition

approximates to that of cantharidinphenylhydrazone, $C_{16}H_{18}N_2O_3$; before it attains this composition, however, decomposition sets in.

The author is investigating the constitution of this substance.

W. J. P.

Compounds of Hydrogen Diaminechromium Thiocyanate with Nitrogenous Bases. By O. T. Christensen (*J. pr Chem.* [2], **45**, 356—376; compare this vol., p. 798).—*Methylamine hydrogen diaminechromium thiocyanate*, $NH_2Me,HSCN,Cr(NH_3)_2(SNC)_3 + H_2O$, is precipitated when a saturated aqueous solution of ammonium diaminechromium thiocyanate is added to a concentrated solution of methylamine hydrochloride; it forms slender, microscopic, red needles, and is sparingly soluble in water, but easily in 96 per cent. alcohol; concentrated ammonia dissolves it slowly, the ammonia replacing the methylamine. *Dimethylamine hydrogen diaminechromium thiocyanate*, $NHMe_2,HSCN,Cr(NH_3)_2(SNC)_3$, is similarly prepared from dimethylamine hydrochloride; it crystallises in microscopic, purple prisms, and is less soluble, both in alcohol and water, than the methylamine salt; it dissolves in concentrated ammonia. The *trimethylamine* salt, $NMe_3,HSCN,Cr(NH_3)_2(SCN)_3$, is sufficiently sparingly soluble in cold water to be precipitated when dilute solutions of trimethylamine hydrochloride and the thiocyanate are mixed; it crystallises in microscopic, purple prisms or hexagonal tables, and is very sparingly soluble in cold 96 per cent. alcohol; it is more soluble in concentrated ammonia than in water, and is ultimately converted thereby into ammonium diaminechromium thiocyanate. The *ethylamine* salt, $NH_2Et,HSCN,Cr(NH_3)_2(SCN)_3$, is precipitated when concentrated solutions of ethylamine hydrochloride and the thiocyanate are mixed and excess of hydrochloric acid is added; it crystallises from hot water in slender, purple needles which dissolve sparingly in cold water, freely in cold alcohol, and not at all in absolute ether. The *amylamine* salt,

$$C_5H_{11}\cdot NH_2,HSCN,Cr(NH_3)_2(SCN)_3,$$

separates from a mixture of concentrated solutions of amylamine hydrochloride and the thiocyanate; it crystallises in microscopic needles and tables, and is very easily soluble in alcohol. It is to be noted that the hydrogen diaminechromium thiocyanates of primary amines are readily soluble in cold 96 per cent. alcohol, while those of secondary amines are less soluble, and those of tertiary amines still less soluble in this solvent; the author suggests this as a practical differentiation.

Aniline hydrogen diaminechromium thiocyanate,

$$NH_2Ph,HSCN,Cr(NH_3)_2(SCN)_3,$$

precipitated from dilute solutions of aniline hydrochloride and the thiocyanate, crystallises from hot alcohol in microscopic, red, rhombic tables; it dissolves sparingly in cold water, but freely in hot water, cold alcohol, and ammonia. The *orthotoluidine* salt,

$$C_6H_4Me\cdot NH_2,HSCN,Cr(NH_3)_2(SCN)_3,$$

forms thin, four-sided, red, rectangular laminæ, and dissolves easily

in hot water and cold alcohol. The *paratoluidine* salt crystallises in lustrous, red, rhombic tables; it is more sparingly soluble in cold water than the ortho-salt, and dissolves easily in hot water and cold alcohol. The *phenylhydrazine* salt,

$$NHPh{\cdot}NH_2,HSCN,Cr(NH_3)_2(SCN)_3 + 2H_2O,$$

forms microscopic, purple, tabular crystals, and dissolves very slightly in cold water, but more freely in hot water and cold alcohol. The *pyridine* salt, $C_5NH_5,HSCN,Cr(NH_3)_2(SCN)_3$, forms purple, microscopic, four-sided prisms; it is nearly insoluble in cold water, and only sparingly soluble in hot water and cold alcohol. The *picoline* salt, $C_5NH_4Me,HSCN,Cr(NH_3)_2(SCN)_3$, crystallises in purple laminæ; it is very little soluble in cold water, and only sparingly so in hot water and cold alcohol. The *quinoline* salt,

$$C_9NH_7,HSCN,Cr(NH_3)_2(SCN)_3,$$

forms microscopic, red, rhombic laminæ, practically insoluble in cold water, sparingly soluble in hot water and cold alcohol. The *morphine* salt, $C_{17}H_{19}NO_3,HSCN,Cr(NH_3)_2(SCN)_3$, is a bright-red, crystalline powder, and is nearly insoluble in cold water, but somewhat soluble in cold alcohol. The *quinine* salt,

$$C_{20}H_{24}N_2O_2[HSCN,Cr(NH_3)_2(SCN)_3]_2 + 2H_2O,$$

is a bright-red, crystalline powder; it is less soluble in hot water than the morphine salt, and more so than the strychnine salt; it is also more soluble in alcohol than the morphine salt. The *strychnine* salt, $C_{21}H_{22}N_2O_2,HSCN,Cr(NH_3)_2(SCN)_3$, forms a red, crystalline precipitate, and is very sparingly soluble in cold alcohol and in water. The *pilocarpine* salt, $C_{11}H_{16}N_2O_2,HSCN,Cr(NH_3)_2(SCN)_3$, crystallises from hot alcohol in long, red needles, thus differing considerably in appearance from the salts of the other alkaloïds. The *cocaïne* salt,

$$C_{17}H_{21}NO_4,HSCN,Cr(NH_3)_2(SCN)_3,$$

crystallises from hot water and from hot alcohol in red laminæ. The *atropine* and *hyoscyamine* salts were also prepared. The *pentamethylenediamine* salt, $C_5H_{10}(NH_2)_2,[HSCN,Cr(NH_3)_2(SCN)_3]_2 + 2H_2O$, crystallises in lustrous, red laminæ, dissolves very sparingly in cold water and alcohol, but more easily in hot water, by which it is speedily decomposed.

The author remarks that the exactness with which it is possible to determine the chromium in these thiocyanates renders them useful compounds by means of which to determine the character of an alkaloïd.

Luteocobalt diaminechromium thiocyanate,

$$Co(NH_3)_6(SCN)_3,[Cr(NH_3)_2(SCN)_3]_3,$$

is obtained as a bright-red precipitate consisting of microscopic tables when solutions of luteocobalt nitrate and ammonium diaminechromium thiocyanate are mixed together; it is practically insoluble in cold water and cold alcohol. Similar salts were obtained from chloropurpureochromium chloride, chloropurpureocobalt chloride, and chlorochromiumtetramine chloride.

Cadmium diaminechromium thiocyanate,

$$Cd(SCN)_2,[Cr(NH_3)_2(SCN)_3]_2 + H_2O,$$

is a red, crystalline powder, almost insoluble in cold water, and only sparingly soluble in hot water and hot alcohol.

The author makes some general remarks as to the possible structure of these complex thiocyanates, and concludes by pointing out that the above salts seem to show that when the nitrogen in the base is attached to three carbon atoms, or by three valencies to one carbon atom, the thiocyanate is sparingly soluble in cold alcohol, whereas when the nitrogen is only attached to one carbon atom, after the manner of a primary amine, the thiocyanate is easily soluble in cold alcohol. A. G. B.

The Compound $C_{36}H_{28}N_4O_6$ obtained by the Action of Sodium Ethoxide on Ethyl Hippurate. By L. Rügheimer (*Ber.*, **25**, 1568—1572; compare Abstr., 1889, 1210).—The compound $C_{36}H_{28}N_4O_6$, when boiled with an excess of acetic anhydride, yields a colourless diacetyl derivative, $C_{40}H_{32}N_4O_8$, which crystallises from alcohol in delicate needles, and melts at 201—202°; it also forms a dibromo-derivative, $C_{36}H_{24}Br_2N_4O_6$ or $C_{36}H_{26}Br_2N_4O_6$, melting at 240—241°; and the latter, on treatment with zinc-dust and acetic acid, gives a colourless compound melting at 183—184°, resembling in its behaviour dihydroxybenzamidopyrroline (Abstr., 1889, 391); the formation of such a compound as the latter is conceivable if the compound $C_{36}H_{28}N_4O_6$ is disanhydrotetrabenzamidotetrahydroxyoctene, as previously suggested (*loc. cit.*). A. R. L.

Desylacetic Acid. By F. Klingemann (*Annalen*, **269**, 131—142; compare Japp and Klingemann, Trans., 1890, 662).—*Diphenylcrotolactone*, $\begin{matrix}CH_2—CO\\ |\\ CPh{:}CPh\end{matrix}>O$, is formed, with liberation of water, when the desylacetic acid (*β*-phenyl-*β*-benzoylpropionic acid) described by Meyer and Oelkers (Abstr., 1888, 703) and by Knoevenagel (Abstr., 1888, 706) is distilled under reduced pressure; it crystallises from a mixture of light petroleum and benzene in slender, colourless needles melting at 151·5°.

Two compounds are formed when desylacetic acid is heated with phenylhydrazine; they are separated by treatment with alcohol. The one crystallises from alcohol, in which it is moderately easily soluble, in colourless, rhombic plates, $a : b : c = 0{\cdot}86112 : 1 : 0{\cdot}43096$, melts at 110°, and has the composition $C_{22}H_{18}N_2O$; it is probably an anilidodiphenylpyrrolone of the constitution $\begin{matrix}CH_2—CO\\ |\\ CPh{:}CPh\end{matrix}>N{\cdot}NHPh$. The second compound is only sparingly soluble in alcohol, crystallises from glacial acetic acid in colourless needles, and melts at 243°; it has the composition $C_{44}H_{34}N_4O_2$.

When the compound just described as anilidodiphenylpyrrolone is treated with bromine in carbon bisulphide solution, it is converted into the colourless substance of the composition $C_{44}H_{34}N_4O_2$; on re-

duction with sodium and amyl alcohol, it yields aniline and *diphenylpyrrolidone*, $\begin{matrix}CH_2\text{——}CO\\ |\\ CHPh\cdot CHPh\end{matrix}>NH$; the last-named compound separates from alcohol in colourless crystals melting at 207°.

Diphenylpyrrolone, $\begin{matrix}CH_2\text{—}CO\\ |\\ CPh{:}CPh\end{matrix}>NH$, is formed when diphenylcrotolactone is heated with excess of alcoholic ammonia at 150°; it crystallises in long, almost colourless needles, and melts and darkens at 188—189°.

Triphenylpyrrolone, $\begin{matrix}CH_2\text{—}CO\\ |\\ CPh{:}CPh\end{matrix}>NPh$, is obtained, together with a colourless, crystalline substance of the composition $C_{44}H_{32}N_2O_2$, when desylacetic acid is heated with aniline; it crystallises from acetic acid in compact, colourless crystals melting at 189—190°.

F. S. K.

Derivatives of α-Phenylquinoline. By E. Murmann (*Monatsh.*, **13**, 58—72).—α-Phenylquinoline is readily sulphonated when it is dissolved in an equal weight of sulphuric acid, and the solution is heated with its own weight of fuming acid, previously added to twice its weight of ordinary acid, until a small quantity withdrawn from the liquid and dissolved in water gives no turbidity with ammonia. The product consists of a mixture of the para- and meta-sulphonic acids, which can be readily separated by the fractional crystallisation of their barium salts, that of the para-compound being relatively very insoluble in water.

Quinoline-α-phenylparasulphonic acid, $C_{15}H_{11}NSO_3 + H_2O$, crystallises from hot water in yellow scales, melts far above 300°, gives a *barium salt* which crystallises in glistening white scales, and an *ammonium salt* which crystallises in anhydrous scales or plates. When the acid is fused with potash, it yields parahydroxy-α-phenylquinoline (m. p. 238; compare Weidel, *Monatsh.*, **8**, 130).

Quinoline-α-phenylmetasulphonic acid, $C_{15}H_{11}NSO_3$, crystallises from hot water in anhydrous, yellow grains, melts far above 300°, and furnishes the salts $(C_{15}H_{10}NSO_3)_2Ba + 1\frac{1}{2}H_2O$, crystallising in needles, $C_{15}H_{10}NSO_3K + H_2O$, crystallising in yellowish plates, and dissolving readily in water, and $C_{15}H_{10}NSO_3Ag + 2\frac{1}{2}H_2O$, which crystallises in drusy masses of slender needles. On fusing this acid with potash, metahydroxy-α-phenylquinoline (m. p. 156°) was obtained (compare Miller and Kinkelin, *Ber.*, **18**, 1908), from which the following derivatives were prepared:—The *hydrochloride*, $C_{15}H_{11}NO,HCl + 1\frac{1}{2}H_2O$, which crystallises in drusy masses of slender needles, is sparingly soluble in water, and melts at 228° (uncorr.); the *acetyl derivative*, $C_{15}H_{10}NOAc$, which crystallises in short, flat, colourless needles, melts at 92° (uncorr.), and is reduced by tin and hydrochloric acid to the *tetrahydride*, $C_{15}H_{15}NO$; the latter melts at 113—115° (uncorr.), and forms a *hydrochloride*, $C_{15}H_{15}NO,HCl$, which crystallises in cubes, melts at 187—188° (uncorr.), and on fusion with potash gives metahydroxybenzoic acid (m. p. 199·5°).

G. T. M.

Nomenclature of Pyrazolones. By L. Lederer (*J. pr. Chem.* [2], **45**, 413—414).—Commenting on Knorr's objection to the terms iso-pyrazolone and hydropyrazolone (this vol., p. 732), the author maintains that no new principle is introduced by their adoption. On the contrary, Knorr's term for reduced pyrazolone, pyrazolidone, is an entirely new departure, and will create the confusion for which he tries to make the author responsible. A. G. B.

Ethyl Malonate Phenylhydrazide and 1-Phenyl-3 : 5-pyrazolidone. By A. Michaelis and R. Burmeister (*Ber.*, **25**, 1502—1513; compare Abstr., 1891, 1068).—The substance obtained by the action of phenylhydrazine on ethyl chloromalonate, $CHCl(COOEt)_2$, is now shown to be *ethyl malonate phenylhydrazide*, $COOEt\cdot CH_2\cdot CO\cdot N_2H_2Ph$, for it is identical with the substance formed when ethyl malonic chloride, $COOEt\cdot CH_2\cdot COCl$, is treated with phenylhydrazine, and when warmed with excess of phenylhydrazine, it yields malonic diphenylhydrazide, $CH_2\cdot(CO\cdot N_2H_2Ph)_2$. It melts at 90°, dissolves sparingly in cold ether, more readily in hot, and readily in benzene, alcohol, and acetic acid; it is insoluble in light petroleum. It dissolves also in hot water, from which it crystallises in large, colourless needles. It dissolves in cold strong sulphuric acid, giving a pale-violet colour, and if a fragment of potassium dichromate is added, reddish or violet streaks are formed (Bülow's reaction for hydrazides); its alcoholic solution stains the skin purple. It reduces Fehling's solution. When heated with strong hydrochloric acid, it is decomposed, phenylhydrazine hydrochloride being formed. With phenyl isocyanate and thiocarbimide, it yields respectively a semicarbazide, $NHPh\cdot CO\cdot N(CO\cdot CH_2\cdot COOEt)\cdot NHPh$, melting at 158°, and a thiosemicarbazide melting at 141°. When the former is dissolved in cold alcoholic potash, and dilute hydrochloric acid added, a substance, $C_{16}H_{13}N_3O_3 + H_2O$, is precipitated, which crystallises from dilute alcohol in white, spherical, crystalline aggregates, melts at 166°, and is probably the semicarbazide of 1-phenyl-3 : 5-pyrazolidone, $\begin{matrix}CO\cdot NPh\\ |\\ CH_2\cdot CO\end{matrix}>N\cdot CO\cdot NHPh$.

On adding sodium nitrite to an acetic acid solution of the phenylhydrazide, *ethyl malonate nitrosophenylhydrazide*,

$$COOEt\cdot CH_2\cdot CO\cdot NH\cdot NHPh\cdot NO,$$

is obtained as yellow needles, which can be crystallised from alcohol. It melts at 85°, decomposes gradually when kept, gives Liebermann's reaction, and reduces Fehling's solution.

1-*Phenyl*-3 : 5-*pyrazolidone*, $\begin{matrix}NPh\cdot CO\\ |\\ NH\cdot CO\end{matrix}>CH_2$, is formed when ethyl malonate phenylhydrazide is dissolved in cold aqueous potash, and dilute hydrochloric acid added. It crystallises from alcohol in lustrous plates melting at 192°, and dissolves sparingly in ether and in cold water and alcohol, more readily in hot water and alcohol, and readily in alkalis. It reduces Fehling's solution, and no longer gives Bülow's reaction. It dissolves in hot strong hydrochloric acid, but when the solution is heated to 170° in a sealed tube, it is decomposed,

carbonic anhydride, aniline, and phenylhydrazine being formed. It probably has the constitution given above, yields metallic salts, and forms condensation products with aldehydes and ketones. The *ammonium salt*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NH\cdot CO}\end{matrix}\!\!>\!\mathrm{CH{\cdot}NH_4}$, is formed when the pyrazolidone is dissolved in strong ammonia; it crystallises in white plates and melts at 165°. The *potassium* and *sodium salts* are easily obtained, but crystallise badly. The *lead salt*, $(C_9H_7N_2O_2)_2Pb$, is precipitated as a white, amorphous powder when hot solutions of the ammonium salt and of lead acetate are mixed.

1-*Phenyl*-4-*benzylidene*-3 : 5-*pyrazolidone*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NH\cdot CO}\end{matrix}\!\!>\!\mathrm{C{:}CHPh}$, is formed when the phenylpyrazolidone is heated with benzaldehyde. It forms dark-red plates, dissolves readily in hot acetic acid, sparingly in hot alcohol, not at all in water, ether, and chloroform, and is decomposed by hot aqueous soda. It is also formed, together with benzylidenephenylhydrazone, when malonic diphenylhydrazide is heated with benzaldehyde.

1-*Phenyl*-4-*isopropylene*-3 : 5-*pyrazolidone*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NH\cdot CO}\end{matrix}\!\!>\!\mathrm{C{:}CMe_2}$, is obtained when the phenylpyrazolidone is boiled with acetone. It forms yellow needles, melts at 164°, dissolves in acetone and hot alcohol and ether, and is insoluble in water.

1-*Phenyl*-3 : 5-*pyrazolidone*-4-*azobenzene*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NH\cdot CO}\end{matrix}\!\!>\!\mathrm{CH{\cdot}N_2Ph}$, is obtained by adding diazobenzene chloride to a cooled solution of the phenylpyrazolidone in dilute aqueous soda, and acidifying the solution with dilute hydrochloric acid. It crystallises from hot acetic acid in lustrous, golden plates, melts at 232°, dissolves readily in hot acetic acid and dilute soda, sparingly in ether and alcohol, and is insoluble in water.

1-*Phenyl*-4-*isonitroso*-3 : 5-*pyrazolidone*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NH\cdot CO}\end{matrix}\!\!>\!\mathrm{C{:}NOH} + \mathrm{H_2O}$, is obtained when sodium nitrite is added to a cooled solution of the phenylpyrazolidone, and the mixture poured into cooled dilute sulphuric acid. It crystallises from hot water in dark red needles, melts at 182°, dissolves readily in hot water, acetic acid, and alcohol, and does not give Liebermann's reaction.

1-*Phenyl*-2 : 4-*dibenzoyl*-3 : 5-*pyrazolidone*, $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NBz\cdot CO}\end{matrix}\!\!>\!\mathrm{CHBz}$, or $\begin{matrix}\mathrm{NPh{\cdot}CO}\\ |\\ \mathrm{NBz\cdot CO}\end{matrix}\!\!>\!\mathrm{C{:}CPh{\cdot}OH}$, is obtained by boiling the phenylpyrazolidone with excess of benzoic chloride. It melts at 111°, dissolves readily in alcohol and ether, is insoluble in soda and dilute acids, and does not reduce Fehling's solution.

When the phenylpyrazolidone is heated for a few minutes with phenylhydrazine, it unites with 1 mol. of the latter to form a substance, $C_{15}H_{16}N_4O_2$, which crystallises from alcohol in white plates melting at 165°. This is not decomposed by alkalis, dissolves in

hot strong, and in cold dilute acids, reduces Fehling's solution, and gives Bülow's reaction. Its constitution is as yet undetermined.

In conclusion, it is pointed out that 1-phenyl-3 : 5-pyrazolidone stands in the same relation to phenylmethylpyrazolone as ethyl malonate does to ethyl acetoacetate. C. F. B.

Furfuran Compounds. By A. Pinner (*Ber.*, **25**, 1414—1427). —In the course of a research on the conversion of nitriles into imido-ethers, the author has observed differences between the compounds of the aromatic and those of the aliphatic series. He has now examined the imido-ethers and amidines derived from furfuran. He designates the radicle C_4OH_3, "furyl," and the radicle C_4OH_3C, "furfur."

Furyl cyanide is easily prepared by shaking furfuraldehyde with free hydroxylamine in aqueous solution, when furfuraldoxime is precipitated as an oil, which soon crystallises. The mixture is allowed to remain all night, and acidified; the crystalline mass dried, cautiously heated to boiling with twice the weight of acetic anhydride, then diluted with water, made alkaline with sodium hydroxide, and the nitrile extracted with ether. It boils at 145—146°.

Furfurimidoethyl ether hydrochloride, $C_4OH_3{\cdot}C(NH){\cdot}OEt,HCl$, is obtained by passing hydrogen chloride through a solution of the above nitrile in the equivalent quantity of absolute alcohol. It forms colourless, nodular, lustrous crystals, is soluble in alcohol, insoluble in ether, melts at 106° with formation of ethyl chloride and the amide of pyromucic acid, and is decomposed by water into ammonium chloride and ethyl pyromucate (α-furfurancarbonate).

Furfurimidoethyl ether is obtained by treating the hydrochloride with potassium carbonate (33 per cent.) and extracting with ether. It boils at 180—181° without decomposition, has a faint characteristic odour, is insoluble in water, and easily soluble in the other usual solvents.

Furfuramidine hydrochloride, $C_4OH_3{\cdot}C(NH){\cdot}NH_2,HCl$, is obtained by treating the above hydrochloride with alcoholic ammonia. It crystallises in large, transparent, lustrous prisms, which contain 1 mol. H_2O, melts at 72°, is very easily soluble in water and alcohol, and insoluble in ether. Attempts to prepare the free amidine resulted in the formation of the amide of pyromucic acid. When boiled for 10—15 minutes with anhydrous sodium acetate and acetic anhydride, it is converted into a compound which the author believes to be *difurylmethylcyanidine*, $C_4OH_3{\cdot}\overset{N}{\underset{N}{<}}\!\!=\!\!\overset{C(C_4OH_3)}{\underset{CMe}{>}}N$. The latter crystallises from dilute alcohol in silky needles, melts at 138°, is sparingly soluble in water, easily so in alcohol and acetic acid, and has only weak basic properties.

Furylmethylhydroxypyrimidine, $C_4OH_3{\cdot}C\overset{N-CMe}{\underset{N:C(OH)}{<}}\!\!>CH$, is obtained by allowing a mixture of furfuramidine hydrochloride, the equivalent quantity of sodium hydroxide, and a slight excess of ethyl acetoacetate to remain for a few days. A thick, crystalline mass is obtained; it is acidified with dilute acetic acid, filtered, and the product crystallised from alcohol. It crystallises in long, silky needles,

melts at 225°, and is easily soluble in alkalis and strong mineral acids.

Furyldimethylhydroxypyrimidine, $C_4OH_3 \cdot C\begin{matrix}\ll\\\gg\end{matrix}\begin{matrix}N-CMe\\N:C(OH)\end{matrix}CMe$, obtained in the same way from ethyl methylacetoacetate, crystallises from alcohol in small, lustrous needles, and melts at 231°.

Furylmethylbenzylhydroxypyrimidine,

$$C_4OH_3 \cdot C\begin{matrix}\ll\\\gg\end{matrix}\begin{matrix}N-CMe\\N:C(OH)\end{matrix}C \cdot CH_2Ph,$$

is obtained by mixing equivalent quantities of sodium hydroxide, furfuramidine hydrochloride, and ethyl benzylacetoacetate, then adding alcohol, and allowing the mixture to remain about eight days. It crystallises in slender, white needles, melts at 238°, is almost insoluble in water, sparingly soluble in alcohol and cold acetic acid, more so in hot acetic acid, and easily in alkalis and strong mineral acids.

Furylphenylhydroxypyrimidine, $C_4OH_3 \cdot C\begin{matrix}\ll\\\gg\end{matrix}\begin{matrix}N-CPh\\N:C(OH)\end{matrix}NH$, obtained by the action of ethyl benzoylacetate on furfuramidine hydrochloride, crystallises in slender, white needles, melts at 256°, and is very sparingly soluble in alcohol and cold acetic acid, more so in hot acetic acid.

When furfuramidine hydrochloride dissolved in twice its weight of water is treated with equivalent quantities of 15 per cent. soda and ethyl oxalacetate, heat is evolved, and on allowing the mixture to remain three days, a crystalline precipitate of *ethoxalylacetylfurfuramidine* is obtained. By adding half the volume of 15 per cent. soda to the mother liquor, allowing it to remain, and acidifying with acetic acid the acid, $C_9H_8N_2O_5$, corresponding with the above ethyl salt, is obtained. Ethoxalylacetylfurfuramidine,

$$C_4OH_3 \cdot C(NH) \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot COOEt,$$

crystallises from acetone in beautiful, transparent prisms, is almost insoluble in water, sparingly soluble in alcohol and cold acetone, easily in hot acetone, begins to blacken at 180°, and melts at 190° with decomposition. The author believes that the acid $C_9H_8N_2O_5$ is *furylhydroxypyrimidinecarboxylic acid*, $C_4OH_3 \cdot C\begin{matrix}\ll\\\gg\end{matrix}\begin{matrix}N \cdot C(COOH)\\N=C(OH)\end{matrix}CH, H_2O$. It is obtained as the sole product if the mixture of furfuramidine hydrochloride and ethyl oxalacetate is boiled with sodium hydroxide, and is also obtained by hydrolysing the above ethyl salt with soda. It crystallises from dilute acetic acid in microscopic prisms, is sparingly soluble in alcohol, cold water, and acetic acid, more so in hot water and acetic acid, melts above 300° with decomposition, and does not lose in weight when heated at 135°. It yields a *silver salt* of the composition $C_9H_4N_2O_4Ag_2$.

The author has examined the action of ethyl oxalacetate on other amidines, and has obtained a pyrimidinecarboxylic acid in every case.

When a mixture of molecular proportions of tolenylamidine (dis-

solved in five times the weight of water), sodium hydroxide (15 per cent.), and ethyl oxalacetate is allowed to remain eight days, a crystalline precipitate is obtained, which is partly soluble in acetone. The soluble portion is *ethoxalylacetyltolenylamidine*,

$$C_6H_4Me\cdot C(NH)\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot COOEt.$$

It crystallises in short, colourless prisms, blackens at 170°, melts at 190° with decomposition, and is easily converted into tolylhydroxypyrimidinecarboxylic acid when treated with sodium hydroxide.

Paratolylhydroxypyrimidinecarboxylic acid,

$$C_6H_4Me\cdot C\lessdot\begin{matrix}N\cdot C(COOH)\\ N=C(OH)\end{matrix}\gtrdot CH,$$

remains insoluble on extracting the product of the above reaction with acetone. It crystallises from acetic acid in small, nodular crystals, and melts at 252° with decomposition.

Naphthamidine, when treated with ethyl oxalacetate in a similar way, yields *β-naphthylhydroxypyrimidinecarboxylic acid*, which crystallises in small prisms, and melts at 167—168° with decomposition.

Methylhydroxypyrimidinecarboxylic acid, $C_6H_6N_2O_3,H_2O$, is obtained in a similar way from acetamidine. It crystallises in small, white needles, is sparingly soluble in water and acids, loses its water at 100°, decomposes at a high temperature, but is unaltered at 300°.

Ethylhydroxypyrimidinecarboxylic acid, $C_7H_8N_2O_3,1\frac{1}{2}H_2O$, crystallises in slender, silky needles, is easily soluble in hot water, sparingly in alcohol and acetone, melts at 216° with decomposition, and loses its water at 100°.

Benzamidine, when treated with carbonyl chloride, yields dibenzamidylcarbamide, which easily loses ammonia, and yields diphenylhydroxycyanidine (Abstr., 1891, 60). A similar reaction takes place in the case of paratolenylamidine, β-naphthamidine, and furfuramidine. The aliphatic amidines do not, however, yield hydroxycyanidine.

Difurylhydroxycyanidine, $C_4OH_3\cdot C\lessdot\begin{matrix}N\cdot C(C_4OH_3)\\ N=C(OH)\end{matrix}\gtrdot N$, is obtained by gradually adding a 20 per cent. toluene solution of carbonyl chloride with constant shaking to a concentrated solution of furfuramidine hydrochloride, and 15 per cent. sodium hydroxide (4 mols.), until carbonic anhydride begins to come off. The granular mass which is obtained is crystallised from alcohol: it forms small, white, flat needles, begins to darken at 250°, and, on further heating, slowly decomposes. It is sparingly soluble in alcohol, easily in alkalis.

Ditolylhydroxycyanidine, $C_6H_4Me\cdot C\lessdot\begin{matrix}N\cdot C(C_6H_4Me)\\ N=C(OH)\end{matrix}\gtrdot N$, obtained in a similar way to the preceding compound, crystallises in slender, satiny needles, is sparingly soluble in alcohol, easily in alkalis, and melts above 300°.

Dinaphthylamidinecarbamide, $CO[NH\cdot C(C_{10}H_7):NH]_2$, is obtained, together with a small quantity of dinaphthylhydroxycyanidine, by treating β-naphthamidine with carbonyl chloride. It crystallises from alcohol in small, nodular aggregates, and does not melt at 300°.

β-Naphthylmethylhydroxypyrimidine, $C_{10}H_7 \cdot C\begin{matrix}<\\>\end{matrix}\begin{matrix}N\text{—}CMe\\N{:}C(OH)\end{matrix}\begin{matrix}>\\>\end{matrix}CH$, is obtained by adding the theoretical quantities of ethyl acetoacetate and sodium hydroxide (15 per cent.) to an aqueous solution of β-naphthamidine, then adding alcohol until a clear solution is obtained, and allowing the mixture to remain eight days. The crystalline precipitate which is formed is collected, and recrystallised from alcohol. It forms long, slender needles, melts at 210°, and is somewhat easily soluble in alcohol.

Naphthyldimethylhydroxypyrimidine obtained in a similar way from ethyl methylacetoacetate, crystallises in lustrous needles or short prisms, is sparingly soluble in alcohol, and melts at 248°.

Naphthylphenylhydroxypyrimidine is obtained in a similar way from ethyl benzoylacetate; it crystallises from acetic acid in short, thin prisms, melts at 265°, and is insoluble in water, very sparingly soluble in alcohol and cold acetic acid, more so in hot acetic acid.

E. C. R.

Tetrazole. By J. A. Bladin (*Ber.*, **25**, 1411—1413).—The author has obtained triazole (this vol., p. 735) by oxidising amidophenyltriazolecarboxylic acid with permanganate in alkaline solution and then eliminating carbonic anhydride from the triazolecarboxylic acid which is first formed. He has now prepared tetrazole in a similar way.

Nitrophenyltetrazolecarboxylic acid, $N\begin{matrix}<\\>\end{matrix}\begin{matrix}N{\cdot}N{\cdot}C_6H_4{\cdot}NO_2\\N{:}C{\cdot}COOH\end{matrix}$, is prepared by boiling phenyltetrazolecarboxylic acid (10 grams) with fuming nitric acid (100 grams) as long as nitrous fumes are evolved. The product is poured into water, and the precipitate separated and dried. It crystallises from acetic acid in colourless leaflets containing 1 mol. of acetic acid, and in needles containing 1 mol. H_2O, melts at 175° to a yellow oil with evolution of gas, and explodes on ignition.

Amidophenyltetrazolecarboxylic acid is obtained by reducing the above nitro-compound with warm stannous chloride and fuming hydrochloric acid. It is purified by dissolving in ammonia and precipitating with sulphuric acid, and melts at 196° with decomposition.

Tetrazole, $\begin{matrix}NH{\cdot}N\\CH{:}N\end{matrix}\begin{matrix}>\\>\end{matrix}N$ or $\begin{matrix}N{\cdot}NH\\CH{\cdot}N\end{matrix}\begin{matrix}>\\>\end{matrix}N$, is obtained as follows:—

Amidophenyltetrazolecarboxylic acid (7 grams) is dissolved in 50 per cent. soda (56 grams) and the warm solution gradually mixed with concentrated permanganate (35—40 grams). When the permanganate is no longer decolorised, the excess is destroyed with alcohol and the mixture filtered. The filtrate is concentrated, acidified with nitric acid, heated to boiling, and silver nitrate added. A colourless silver salt is precipitated. The latter is warmed with hydrochloric acid, the solution filtered from silver chloride, and evaporated to dryness on the water-bath. Tetrazole is obtained as a yellowish, crystalline mass, and is purified by crystallisation from alcohol. It crystallises from toluene in lustrous leaflets, from alcohol

in hard, aggregated leaflets, sublimes before melting, melts at 155°, and is easily soluble in water, alcohol, acetone, and acetic acid, sparingly so in ether, benzene, and toluene. It reddens blue litmus paper, has no basic properties, and gives precipitates with metallic salts. The silver and copper salts explode violently on heating.

E. C. R.

Nicotine. By A. Pinner and R. Wolffenstein (*Ber.*, **25**, 1428—1433).—The authors have attempted to obtain compounds of known constitution from oxynicotine, $C_{10}H_{12}N_2O$ (obtained by the action of hydrogen peroxide on nicotine), by heating it with hydrochloric acid and with barium hydroxide. With hydrochloric acid, a compound, $C_{10}H_{14}N_2O$, which the authors name pseudonicotine oxide, is obtained. With barium hydroxide, nicotine is obtained, together with a non-volatile resin.

Pseudonicotine oxide is prepared as follows:—Oxynicotine is heated with eight times the quantity of fuming hydrochloric acid for 8—10 hours at 140°, the dark-coloured product is made alkaline with soda, and then distilled with steam as long as the distillate is alkaline. The distillate is acidified with hydrochloric acid and evaporated to crystallisation, when the *hydrochloride*, $C_{10}H_{14}N_2O,2HCl$, is obtained. This crystallises from alcohol in white leaflets, melts at 192°, gives, with mercuric chloride, a double salt melting at 212°, and yields a *platinochloride*, $C_{10}H_{14}N_2O,H_2PtCl_6$, which crystallises in small needles and begins to decompose at 120°. The *free base* is obtained by decomposing the hydrochloride with sodium hydroxide and extracting with ether; on evaporating the ether, an oil is left, which quickly turns red on exposure to air. It is soluble in water in all proportions, and is precipitated as an oil by concentrated sodium hydroxide. Besides pseudonicotine oxide, a basic, brownish-black resin, which is not volatile with steam, is also formed.

Dehydronicotine, $C_{10}H_{12}N_2$, is an oil which comes over between 265° and 275°, when freshly-prepared pseudonicotine oxide is distilled. It does not turn red on exposure to air, and is somewhat sparingly soluble in water. The *picrate* forms very small, prismatic crystals, and melts at 208°. The *platinochloride* is orange-coloured, and does not melt at 260°.

The physiological action of pseudonicotine oxide and dehydronicotine is very similar to that of nicotine. The oxygen-free base, $C_{10}H_{12}N_2$, has as intense an action as nicotine itself. Pseudonicotine oxide is about 20 times weaker.

E. C. R.

Conversion of Cupreïne into Quinine. By O. Hesse (*Annalen*, **269**, 143—144).—A reply to Grimaux and Arnaud (this vol., p. 892).

Halogen Derivatives of the Cinchona Alkaloïds. By W. J. Comstock and W. Koenigs (*Ber.*, **25**, 1539—1551).—It has already been shown (Abstr., 1887, 1123) that two isomeric cinchonine dibromides, giving the same dehydrocinchonine on boiling with alcoholic potash, are formed by brominating cinchonine dissolved in a mixture of alcohol and chloroform. The α-modification, $C_{19}H_{22}N_2O$ +

H_2O, crystallises in rhombic pyramids, exhibiting strong double refraction, the extinction being parallel and perpendicular to the base; whilst the β-modification forms lance-shaped leaflets, frequently combined in stellate groups, exhibiting feeble double refraction, the extinction being parallel and perpendicular to their length. Neither of the dibromides appears to be capable of combining with hydrogen bromide.

In the light of Skraup's experiments, the authors now hold the view that only one quinoline residue is present in the cinchona alkaloïds, and that the so-called second complex ($C_{10}H_{16}NO$), which in cinchonine and cinchonidine is combined with a quinoline residue, and in quinine and quinidine with a paramethoxyquinoline residue, consists of hydrogenised benzene and pyridine nuclei combined in a manner similar to that which Merling has suggested for tropine and ecgonine (this vol., p. 358). In support of this hypothesis, the authors cite the inferior stability of the above-mentioned complex, $(C_{10}H_{16}NO)'$, in comparison with that of a quinoline residue; furthermore, whilst Merling (*loc. cit.*) has shown that tropine and ecgonine give tropinic acid, $C_8H_{13}NO_4$, on oxidation, Skraup (*Monatsh.*, **9**, 783; **10**, 39 and 220) has obtained cincholeuponic acid, $C_5NH_8Me(COOH)_2$, on oxidising the cinchona alkaloïds.

A base, $C_{19}H_{22}Cl_2N_2O$, having the same properties as the "dichlorocinchonine" described by Laurent (*Annalen*, **69**, 9), is obtained by passing chlorine through a cooled solution of cinchonine in hydrochloric acid; it is purified by means of its sparingly soluble nitrate. The free base separates from a mixture of chloroform and alcohol in colourless crystals, and, when the temperature is slowly raised, melts at 202—204° with partial decomposition, whilst, if the temperature is quickly raised, it melts at 220° or even 230°. When boiled with alcoholic potash, hydrogen chloride is slowly eliminated, and a crystalline base, probably dehydrocinchonine, melting at 203—205°, is produced.

Dehydrocinchonine dibromide, $C_{19}H_{20}Br_2N_2O$ (or $C_{19}H_{18}Br_2N_2O$), is obtained by brominating at 0° dehydrocinchonine hydrochloride dissolved in a mixture of chloroform and alcohol; the base crystallises in small, transparent prisms, melts at 172—173°, and is readily soluble in alcohol and chloroform, sparingly so in ether.

"Cinchonine chloride," $C_{19}H_{21}N_2Cl$, is thus prepared:—Dry cinchonine hydrochloride (100 grams) is dissolved in dry chloroform (1200 grams), and, to the cooled solution, finely-pulverised phosphorus pentachloride (134 grams), suspended in chloroform, is added; the mixture is then heated on the water-bath for 1—1½ hours. When boiled with alcoholic potash, cinchen, $C_{19}H_{20}N_2$, is obtained; whilst a secondary base, which was not further investigated, is formed when cinchonine chloride is treated with 2 per cent. sodium amalgam at the ordinary temperature; and octohydrocinchen (see below) seems to be produced by heating it with concentrated hydriodic acid in a sealed tube at 240—250°.

"*Hydrobromocinchonine chloride*," $C_{19}H_{22}BrN_2Cl$, is prepared by dissolving cinchonine chloride in nine times its weight of hydrobromic acid (sp. gr. 1·49), saturating the solution with hydrogen bromide at −17°, and placing the mixture aside for several days; when heated

with hydriodic acid (sp. gr. 1·96; 10 parts) at 240—250° for 9—10 hours, octohydrocinchen is produced. The crude base was converted into the *cadmiochloride*, $C_{19}H_{28}N_2,H_2CdCl_4 + H_2O$, which crystallises in stout, faintly-yellowish crystals, and melts at 140—150°; the *platinochloride* was obtained as an oil, whilst the pure base was not prepared.

Dehydrocinchen forms a *dibromide*, $C_{19}H_{18}Br_2N_2$.

Quinine dibromide, $C_{20}H_{24}Br_2N_2O_2$, is obtained by treating quinine dissolved in a mixture of alcohol and chloroform with bromine at 0°, extracting with water, adding ammonia to the aqueous solution, and purifying by crystallisation of the nitrate. The base is sparingly soluble in cold water, somewhat easily in benzene, and crystallises therefrom with 1 mol. C_6H_6, which it slowly loses on exposure to the air. A. R. L.

Alkyl Derivatives of Cinchona Alkaloïds. By A. Claus (*J. pr. Chem.* [2], **45**, 398—401).—The author is surprised that Freund and Rosenstein, in their recent paper (this vol., p. 892), should have alluded to his work on this subject as having been discontinued. The numerous papers published by the author and his pupils on quinolines and their derivatives are all parts of his work on cinchona alkaloïds, and his most recent paper (*Annalen*, **269**, 232) is concerning these alkaloïds. He therefore insists on his prior claim to the subject. A. G. B.

Strychnine. By J. Tafel (*Annalen*, **268**, 229—255; compare Abstr., 1891, 1262).—*Nitrosoisostrychnic acid*,

$$NO\cdot C_{20}H_{21}NO(COOH):NH + H_2O,$$

is formed when the hydrochloride of isostrychnic acid nitrosamine (*loc. cit.*) is treated with ice-cold alcoholic hydrochloric acid, and the mixture then kept at the ordinary temperature until the yellow solid, which is first precipitated, is redissolved. It is precipitated from its solution in soda, on the addition of hydrochloric acid, in yellowish-green needles, and is only very sparingly soluble in hot water, almost insoluble in boiling alcohol, and insoluble in acetone and chloroform; it dissolves freely in alkalis and in glacial acetic acid, and forms salts with strong mineral acids. When its hydrochloric acid solution is treated with tin, a transient, dark-red, and then a slight yellow, coloration is produced; after precipitating the tin with hydrogen sulphide, the colourless filtrate turns violet on exposure to the air, and after neutralising with soda, it gives, with ferric chloride, an intense violet colour, which changes to green on adding more of the reagent. It yields, with nitrous acid, a nitrosamine, but it does not show Liebermann's reaction, and it does not give any volatile base when boiled with 10 per cent soda.

Methylisostrychnic acid, $COOH\cdot C_{20}H_{22}NO:NMe + 2\frac{1}{2}H_2O$, can be obtained by heating anhydrous isostrychnic acid hydriodide with methyl iodide at 100° for two to three hours. It crystallises in long, colourless prisms, loses the whole of its water over sulphuric acid under reduced pressure, and turns brown when heated above 240°, but without melting completely; its alkaline solutions, unlike those of

isostrychnic acid, do not become coloured on exposure to the air. It gives with concentrated nitric acid, containing a trace of nitrous acid, with ferric chloride, and with a little potassium dichromate, a red coloration, the reaction being in every case more delicate than that given by methyltetrahydroquinoline (kairoline) under similar conditions.

Methylisostrychnic acid behaves in many respects like dimethylstrychnine, and also like the dialkylanilines; when warmed with benzaldehyde and zinc chloride, it yields a colourless leuco-compound, which is converted into a beautiful green dye on oxidation; with diazobenzene chloride, it forms an acid azo-dye similar to helianthin.

Ethyl nitrosomethylisostrychnate, $NO{\cdot}C_{20}H_{21}NO(COOEt){:}NH$, is formed when an alcoholic solution of methylisostrychnic acid is saturated with hydrogen chloride, the hydrochloride obtained in this way treated with amyl nitrite in well-cooled, alcoholic solution, and the product decomposed with dilute soda. It crystallises from benzene in green needles, and dissolves freely in chloroform, warm alcohol, and warm benzene, but is only sparingly soluble in ether. Nitrosomethylisostrychnic acid is stable towards dilute soda, and, even when boiled therewith, it does not yield a volatile base; it does not give Liebermann's reaction.

Deoxystrychnine, $C_{20}H_{26}N\lessdot^{CO}_{N}$ + $3H_2O$, is formed, together with resinous compounds, when strychnine is boiled with concentrated hydriodic acid and amorphous phosphorus for 18 hours, but it is obtained in a state of purity only with great difficulty. It is almost insoluble in water, and only sparingly soluble in ether and benzene, but readily in cold ethyl and methyl alcohol; it melts in its water of crystallisation when quickly heated to about 75°, and loses the whole of its water at 100°, or when kept for a long time over sulphuric acid under reduced pressure; the anhydrous compound melts at 172°, distils without decomposition, and is readily soluble in alcohol, benzene, chloroform, and ethyl acetate, but more sparingly in hot light petroleum. It has the characteristic poisonous properties of strychnine, an even more bitter taste, and its solution in concentrated sulphuric acid gives, with potassium dichromate, a bluish-violet coloration, which soon changes to brown; a solution of its hydrochloride is feebly dextrorotatory. Its salts are, generally speaking, more readily soluble than the corresponding strychnine compounds; like the latter, they contain only one equivalent of the acid, and show, with litmus, an acid, with methyl-orange, a neutral, reaction. The *hydriodide*, $C_{21}H_{26}N_2O,HI + H_2O$, crystallises in colourless prisms, loses its water at 120°, and is moderately easily soluble in hot water, but more sparingly in cold water and alcohol. The *dichromate*, $(C_{21}H_{26}N_2O)_2,H_2Cr_2O_7$, crystallises in long, yellow needles, and is only very sparingly soluble in hot water, and almost insoluble in boiling alcohol; it begins to decompose at 170°. The *platinochloride*, $(C_{21}H_{26}N_2O)_2,H_2PtCl_6$, forms small, yellow needles, and is very sparingly soluble in boiling water, by which it is slowly decomposed. The *methiodide*, $C_{22}H_{26}N_2O,MeI$, separates in crystals when an alcoholic solution of deoxystrychnine is treated with excess of methyl iodide; it separates from boiling water in colourless crystals, and is only spar-

ingly soluble in hot alcohol, and insoluble in ether. It is not decomposed by hot soda, but when treated with silver oxide in aqueous solution, it is converted into a strongly alkaline ammonium base, which undergoes intramolecular change on evaporating its aqueous solution, yielding a colourless, neutral, crystalline substance, which the author names *methyldeoxystrychnine*.

Deoxystrychnic acid, $COOH{\cdot}C_{20}H_{26}N{\cdot}NH + H_2O$, can be obtained by heating deoxystrychnine with an alcoholic solution of sodium methoxide at 180° and decomposing the product with sodium carbonate. It crystallises in colourless, microscopic needles, containing 2 mols. H_2O, one of which is lost over sulphuric acid under reduced pressure; the other molecule of water cannot be expelled, because, when the acid is heated at 100°, it is partially converted into deoxystrychnine. It is only sparingly soluble in hot water, although more readily than strychnic acid, and when treated with alcohol it dissolves almost entirely, crystals quickly separating again from the solution; these crystals are only sparingly soluble even in boiling alcohol, and, on cooling the solution, it deposits colourless prisms which contain alcohol. It dissolves freely in alkalis and in concentrated ammonia, and the solutions do not become coloured on exposure to the air: when treated with acids, it yields salts of deoxystrychnine, and with potassium dichromate and dilute sulphuric acid it gives an intense red coloration. When a well-cooled solution of sodium deoxystrychnate is treated with sodium nitrite and hydrochloric acid, the hydrochloride of the *nitrosamine* is precipitated as a yellowish resin, which separates from hot water in microscopic needles and gives Liebermann's reaction.

The above observations show that strychnine derivatives behave in many respects just like derivatives of tetrahydroquinoline, and probably contain a tetrahydroquinoline nucleus. F. S. K.

Nitroatropine. By A. Einhorn and L. Fischer (*Ber.*, **25**, 1390—1391).—*Nitroatropine* is obtained by gradually adding atropine (10 grams) to a mixture of concentrated nitric acid (20 c.c.) and sulphuric acid (20 c.c.), cooled to 0°. After remaining 1—2 hours, the mixture is poured on to ice, and potassium carbonate added. The nitroatropine separates as an oil and is extracted with ether. The *hydrochloride*, obtained by dissolving it in alcoholic hydrogen chloride, crystallises from absolute alcohol, decomposes at 235°, and is sparingly soluble in absolute and dilute alcohol, methyl alcohol, chloroform, and acetic acid.

When nitroatropine is boiled with hydrochloric acid, it yields an acid which, on oxidation with alkaline permanganate, is converted into paranitrobenzoic acid (m. p. 290°). E. C. R.

Action of Hypochlorous Acid on Tropine. By A. Einhorn and L. Fischer (*Ber.*, **25**, 1391—1394).—If an aqueous solution of tropine (7·5 grams) is added to a solution of hypochlorous acid, prepared by the action of boric acid on sodium hypochlorite, and the mixture allowed to remain 1—2 days in the dark, a white precipitate is obtained. The latter is filtered off, washed with water, and its

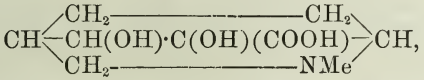
ethereal solution shaken with soda. On concentrating the solution, large, prismatic crystals are obtained, which melt at 111°, and sublime unchanged. The compound has the composition $C_7H_6NCl_5O$, and the authors believe it is an ethereal salt of hypochlorous acid, $C_6H_5NCl_4{\cdot}CH{\cdot}OCl$. One chlorine atom is easily displaced, and by boiling with absolute alcohol, a compound of the formula

$$C_6H_5NCl_4{\cdot}CH{\cdot}OH$$

is obtained, which separates in small, white crystals and melts at 108°. When warmed on the water-bath with hydrochloric acid, it dissolves with evolution of chlorine. The hydrochloride of the new compound crystallises in lustrous, white plates, melts at 162°, and when treated with water, is decomposed into hydrogen chloride and the compound melting at 108°. The authors have made attempts to reduce the compound melting at 108°, but at present have obtained no definite results.

E. C. R.

Dihydroxyanhydroecgonine. By A. Einhorn and B. Rassow (*Ber.*, **25**, 1394—1400).—*Dihydroxyanhydroecgonine*,



is obtained as follows:—A solution of anhydroecgonine hydrochloride (10 grams) in 1500 c.c. of water made slightly alkaline with sodium carbonate is gradually added to 778 c.c. of a 1 per cent. solution of potassium permanganate. The temperature must not be allowed to rise above 1°. The mixture is filtered, acidified with hydrochloric acid, and concentrated on the water-bath; the acid oxidation products are precipitated with baryta, and the mixture treated with carbonic anhydride and filtered. The filtrate is evaporated to a syrup and extracted with methyl alcohol. The crude product is converted into hydrochloride, decolorised with animal charcoal, evaporated to a syrup, allowed to crystallise, dried on porous plates, and recrystallised from dilute alcohol. The *hydrochloride* forms small, white crystals, and melts at 251°.

Dihydroxyanhydroecgonine is obtained by boiling the methyl salt with water for 24 hours, and then precipitating by adding alcohol to the aqueous solution. It decomposes at 280°, is easily soluble in water and methyl alcohol, sparingly in methylated spirit, and insoluble in absolute alcohol and ether. With picric acid, it gives a precipitate of slender, yellow needles; it gives no precipitate with ammoniacal copper solution. The *methyl salt* is obtained by passing hydrogen chloride into a solution of the dihydroxy-acid in methyl alcohol; the alcohol is distilled off, the residue poured into water, and the methyl salt precipitated with potassium carbonate and extracted with chloroform. It crystallises from ether in well-formed, prismatic tables, and melts at 138—139°. The *hydrochloride*, *nitrate*, and *sulphate* are very easily soluble in water. The *platinochloride* crystallises in reddish-yellow needles, and melts at 210°.

When the finely-powdered methyl salt is warmed on the water-bath for some hours with 3—4 times the quantity of benzoic chloride, two

alkaloïds are obtained, one yielding a sparingly soluble hydrochloride and nitrate, the other, easily soluble salts. They are separated by means of the nitrates.

Methyl salt of benzoyldihydroxyanhydroecgonine is obtained from the easily soluble nitrate, which crystallises in beautiful, large, lustrous tablets, and melts at 215—216°, by decomposing it with soda and extracting with ether. It forms slender, white needles when precipitated from its aqueous solution by alcohol, and melts at 107—108°. The *hydrochloride* melts at 202—203° with decomposition; the *aurochloride* crystallises in slender, lustrous needles, and melts at 172—173°; the *platinochloride* crystallises in needles, and melts at 207—208°.

Methyl salt of dibenzoyldihydroxyanhydroecgonine is obtained from the sparingly soluble nitrate mentioned above, which crystallises in slender needles and melts at 189—190°, by shaking it, suspended in water, with sodium carbonate and ether until it all dissolves. It is precipitated from alcohol by water in slender needles, and melts at 99—100°. Both the free alkaloïd and its salts are very easily decomposed with evolution of benzoic acid, so that they have not been obtained in a perfectly pure condition. The *hydrochloride* melts at 280°, the *platinochloride* at 205°, and the *aurochloride* at 208°.

E. C. R.

Pinnaglobin, a New Globulin. By A. B. Griffiths (*Compt. rend.*, **114**, 840—842).—The blood of *Pinna squamosa* is white, but when exposed to the air becomes brownish. It contains a new globulin, *pinnaglobin*, which is precipitated from the clarified serum by alcohol, dissolved in a dilute aqueous solution of magnesium sulphate, precipitated again by saturating the liquid with magnesium sulphate, washed with strong magnesium sulphate solution, and then treated with water, in which it dissolves, owing to the magnesium sulphate still adhering to it. The solution is heated at 56° in order to coagulate some proteïds, and the pinnaglobin is precipitated from the filtrate by the addition of alcohol, washed with water, and dried, first at 60° and afterwards in a vacuum.

Pinnaglobin has the composition C, 55·07; H, 6·24; N, 16·24; Mn, 0·35; S, 0·81; O, 21·29 = 100, and, like hæmocyanin, exists in two states, oxypinnaglobin and reduced or ordinary pinnaglobin. It combines with methane, forming a greenish product, with acetylene, forming a greyish product, and with ethylene forming a reddish compound, but it does not combine with carbonic oxide or with nitric oxide. 100 grams of pinnaglobin absorb 162 c.c. of oxygen at 0° and 760 mm.; pinnaglobin and oxypinnaglobin give no absorption spectra, but the specific rotatory power of the former is $[\alpha]_D = -61°$.

The ash of the blood of *Pinna squamosa* has the composition—

MnO_2.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	SO_3.	Cl.
0·19	3·70	1·83	4·86	44·02	4·79	2·73	37·88

C. H. B.

Peptone Salts of Glutin. By C. Böttinger (*Ber.*, **25**, 1500—1501; compare C. Paal, this vol., p. 895).—On heating mechanically

purified calf skin with water for six hours at 150°, a hygroscopic, readily soluble compound is formed which is a conversion product of gelatin. On boiling this substance for four hours with very dilute hydrochloric acid (0·2—0·5 per cent. of the dried substance), a colourless compound is formed which has a sweet taste and an odour resembling that of molasses. The insoluble portion of the skin amounts to 7—14 per cent., and consists of mineral matter, fat, and nitrogenous compounds. J. B. T.

Oxygen in Oxyhæmoglobin Crystals. By C. Bohr and S. Torup (*Chem. Centr.*, 1892, i, 321; from *Skand. Arch. Physiol.*, **3**, 69).—Hæmoglobin in solution has been found to absorb 1·5—1·6 c.c. of oxygen per gram, but the quantity seems to depend on the concentration of the solution. The dry crystals do not contain nearly so much free oxygen, 0·40, 0·33, and 0·39 c.c. being obtained in three experiments, whereas the solution of the same specimen of hæmoglobin contained 0·99 and 1·19 c.c. of oxygen. J. W. L.

Formation of Oxyhæmoglobin from Hæmatin and a Proteïd. By H. Bertin Sans and J. Moitessier (*Compt. rend.*, **114**, 923—926).—Defibrinated blood is mixed with ether, and the well-drained coagulum boiled with alcohol of 95° containing 8 to 10 per cent. of tartaric acid. A deep brown liquid is thus obtained containing hæmatin and a proteïd resulting from the decomposition of oxyhæmoglobin, and if excess of ether is added, hæmatin is precipitated, and the proteïd remains in solution. The latter shows no trace of an absorption band.

If an alcoholic solution of the hæmatin is mixed with the aqueous solution of the proteïd and diluted with water, the liquid shows the same spectrum as blood that has been treated with concentrated tartaric acid solution. If a 1 per cent. solution of sodium hydroxide is added very gradually, the spectrum of acid methæmoglobin is seen at the point of neutrality. If the liquid is made very slightly alkaline, the characteristic spectrum of alkaline methæmoglobin is observed. On the addition of a few drops of ammonium sulphide, the band of hæmoglobin appears, and, if air is blown into the liquid, oxyhæmoglobin is formed. Similar formation of hæmoglobin results from the action of hydrogen sulphide on the slightly acid methæmoglobin solution. The hæmoglobin thus formed combines with carbonic oxide, and shows the characteristic spectrum.

The alcoholic solution of hæmatin alone gives no hæmoglobin under the same conditions.

Precisely similar results are obtained with crystallised oxyhæmoglobin. It seems clear that hæmatin unites with the proteïd derived from oxyhæmoglobin, and forms methæmoglobin, which is afterwards readily converted into oxyhæmoglobin. C. H. B.

Physiological Chemistry.

Physiological Oxidation. By O. Nasse (*Chem. Centr.*, 1892, i, 173; from *Naturforsch. Gesell. Rostock*).—Benzaldehyde, when shaken with an aqueous solution of copper sulphate in the presence of the least possible quantity of air, acts as a reducing agent, and copper is precipitated; if sulphur be present, copper sulphide will be formed. On the other hand, if oxidisable substances are shaken with benzaldehyde, water, and air, they are oxidised. Water becomes separated into hydroxyl and hydrogen; the former replaces hydrogen in the oxidisable substance, and the hydrogen unites with any organic sulphur which may be present, or precipitates copper from copper sulphate, or attacks the oxygen molecules of the air, and so makes oxygen atoms available for purposes of oxidation. Similar processes have been observed to take place in protoplasm. J. W. L.

Metabolism in Pigs Fed with Corn Cockle. By C. Kornauth and A. Arche (*Landw. Versuchs-Stat.*, **40**, 177—202).—Whilst the seeds of corn cockle (*Agrostemma githago*) are unanimously held by scientific men to be unsuited, on account of their poisonous nature, for feeding, practical agriculturists do not generally take this view, and many Hungarian farmers fatten pigs almost exclusively with offal consisting largely of this seed. Many experiments have been made to ascertain the effect of feeding with the seeds, but the results have always been uncertain. Pusch thinks it is injurious, under some conditions, but that the poisonous action of the seeds varies, the variation being due to the weather and the nature of the soil; and, further, that the injurious action decreases as the feeding is continued, so that, finally, it will be quite harmless. Taking all the results together, it cannot be considered as proved that, with normal feeding, the seeds are injurious.

In the authors' experiments three pigs were fed for four weeks on offal containing 46 per cent. of corn cockle. Two rabbits, fed at the same time, ate the other constituents, leaving the corn cockle. When the offal was ground, the rabbits ate the whole without injury. Having found that no injurious effect was produced when the whole seeds were consumed, various extracts were prepared and injected subcutaneously. This also was without effect. Systematic experiments were next made in which pigs were fed with a mixture of known amounts of corn cockle, barley and maize. The results of the experiments, which are given in tables showing the increase of live weight, composition of food and fæces, amounts of various constituents digested, &c., point to the following conclusions:—

Feeding with corn cockle has no injurious effect on young pigs. When, for instance, 70 per cent. is employed (an amount which would never occur in practice), the growth of the pigs is diminished, but there was no poisonous action, the depression being due to the lessened appetite caused by the bitter food. The deposition of

albumin was diminished, but the deposition of fat rather increased, owing to the lessened production of carbonic anhydride in respiration. The food was used up to the same extent as other food. The flesh produced with corn cockle feeding was normal. The amount of corn cockle required to produce a given increase in live weight is greater than the weight of food free from corn cockle, but not by any means in the proportion corresponding with the low price of the latter, so that this is to be considered as quite suitable for fattening.

N. H. M.

Action of Oxalic Acid and its Derivatives on the Animal Economy. By P. Krohl (*Chem. Centr.*, 1892, i, 177—178; from *Arb. Pharmakol. Inst. Dorpat*, **7**, 131—156).—Sodium oxalate, sodium malonate, ammonium oxalurate, and oxamide cause glycosuria, accompanied by an interruption of the oxidation processes, and carbonic oxide is formed, either in the free state or in combination, as the group —CO·CO—. Since hydrogen cyanide is oxidised to oxamide by hydrogen peroxide, experiments were made to see if it could be employed as an antidote in the case of hydrogen cyanide poisoning.

These experiments were successful, and hydrogen cyanide, in larger quantity than the fatal dose, was administered to dogs and cats, and its effect stayed by means of hydrogen peroxide. The experiment could be made daily for weeks together without permanently injuring the animal. Moreover, hydrogen cyanide could not be detected in the urine after application of hydrogen peroxide, whereas it is present in ordinary cases of hydrogen cyanide poisoning. J. W. L.

Chemistry of Vegetable Physiology and Agriculture.

Accumulation of Atmospheric Nitrogen in Cultivations of Bacillus radicicola. By M. W. Beyerinck (*Meded. Konink. Akad. Wetens.* [3], **8**, 460—475).—The results of the author's earlier experiments with cultivations of *B. radicicola* did not show any gain of nitrogen at the expense of the air (Abstr., 1891, 1539). It was shown that peptone, and also, but much less readily, asparagine, ammonium sulphate, and potassium or sodium nitrates, can serve as sources of nitrogen, whilst nitrites, in all states of dilution, seem to act injuriously, and never give rise to growth. It is now found that, with more favourable conditions, especially as regards nutrition and temperature, the bacillus can be made to develop; at the same time, the nutritive solutions in which they grow gain nitrogen. The experiments were carried out as follows:—

Horse beans were allowed to germinate, the stems cut off, and 100 grams (of stems) boiled for a short time with 1 litre of water. 100 c.c. of this liquid was put into each of 12 Kjeldahl's flasks, and 1·5 per cent. of cane sugar added to each. Some of the flasks (Experiments 1—3) had, besides, 0·3—0·1 gram of potassium mono-

phosphate. The contents of the flasks were infected with *B. radicicola*, isolated from the nodules of Windsor beans. The flasks were kept in a box, to which only a little light had access; the temperature was generally between 5° and 12°, but on rare occasions was as low as 2° and as high as 15°. Most of the cultivations showed turbidity in a few days, whilst the check experiments remained clear. The appearances observed during growth are described in detail. At the conclusion the liquids in the flask were evaporated down (in the flasks) at 100° in a current of air. The nitrogen in the residues was then determined by Kjeldahl's method. The results are shown in the following table :—

Expt. No.	1*.	2.	3.	4.	5.	6.
	gram.	gram.	gram.	gram.	gram.	gram.
Infected	0·0058590	0·0061194	0·0069006	0·0082026	0·0075516	0·0079422
Not infected...	0·0049476†	0·0049476	0·0050778	0·0066402	0·0065100	0·0036402
Gain of nitrogen	0·0009114	0·0011718	0·0018228	0·0015614	0·0011416	0·0013020

The gain is, in all cases, only slight, but the experiments lasted for two months only, and the organisms were in full activity when the experiments were stopped.

With the *Robinia* bacilli, which grew more slowly than those of *Vicia faba*, no increase of nitrogen was obtained in eight weeks; but the author expects that his subsequent experiments will give similar results to those described above.

The solutions contained no nitric acid, either at the beginning or at the end of the experiments.

The results show that a gain of nitrogen from the air took place, but the question remains whether it was the free or the combined nitrogen which was utilised. Although the first experiment, in which the air was freed from combined nitrogen before reaching the solution, showed a gain of nitrogen, the author considers a complete proof is wanting, and that it is more probably the combined nitrogen which is taken up by the organisms. Some light may be thrown on the matter by the investigation of other organisms which have the power of depriving the surrounding matter of nitrogen compounds (*loc. cit.*). If it can be shown that with these organisms an accumulation of nitrogen can be effected, it will be more easy to understand why such an important function as the fixation of free nitrogen, being withheld from all higher plants, should not be assigned to lower organisms.

The power which some micro-organisms have of withdrawing nitrogen compounds from solutions so dilute that the roots of higher plants are unable to extract anything is much more intelligible.

* The flasks in this experiment were provided with U-tubes containing dilute sulphuric acid to wash the air before it entered.

† A separate analysis was made in each case. Two solutions were employed, one for Expts. 1—3, the other for the rest.

The fact observed by Hellriegel and Wilfarth, that the plants, and not the soil, gained nitrogen, is, perhaps, due to the absence of a carbohydrate in the ignited soil, although if carbohydrates were present, quicker-growing organisms would have probably developed rather than *B. radicicola*, and thus prevent nitrogen accumulation.

As regards the nitrogenous food of the Papilionaceæ, this must depend entirely on the dying off of the bacteroids in the nodules, as only dead bacteroids seem able to give up as albumin the nitrogen they took up.

The question next arises whether the plant can exercise an influence on the death of the bacteria or on their renewed production. The first question is difficult to answer, whilst, with regard to the second, it is to be expected that a deficit of assimilable nitrogen in the plant will give rise to an excess of carbohydrate, since the formation of albumin must cease, whilst the decomposition of carbonic anhydride goes on. There is every reason to believe that the carbohydrates are beneficial to the bacteria, and enable them to develop more vigorously at the cost of the nitrogen around them. N. H. M.

Fixation of Free Nitrogen by Plants. By T. Schloesing, jun., and E. Laurent (*Ann. Inst. Pasteur*, **6**, 65—115).—The present paper gives a detailed account of the experiments and of the methods and apparatus employed (compare Abstr., 1891, 353; 1892, 378 and 523). The vessels in which the plants were grown were glass cylinders of about 6—7 litres capacity, closed at the bottom and drawn out to a neck at the upper end. They were filled to about one-third with the sand (2—3 kilos.) or soil (2—2·5 kilos.), the upper space serving to contain the mixed gases supplied and for the development of the plants. The cylinder was connected by means of a mercury joint with the rest of the apparatus, consisting of pump, combustion furnace, tube containing acidified asbestos for the absorption of ammonia, &c., of which sketches are given. As the amount of gas which could be used was very limited, it was of importance that its composition should correspond throughout the experiment with the wants of the plants, and arrangements had to be made so that a portion of the gas could be withdrawn from time to time for analysis (only a small amount of gas was used each time, and the nitrogen residue was returned). The excess of oxygen was got rid of by passing a part of the gas over ignited copper, and the deficiency of carbonic anhydride supplied by heating potassium hydrogen carbonate.

In commencing an experiment, after sowing the seeds or adding the nutritive solutions, or soil extracts, and watering, the whole apparatus was exhausted, carbonic anhydride let in, and again exhausted. The cylinder was then surrounded with water at 30—32°, when a slight amount of gas was given off, which was pumped out. The apparatus was again washed out with carbonic anhydride (still at 30—32°) and exhausted; the gas thus recovered was pure carbonic anhydride. Oxygen, nitrogen, and carbonic anhydride (air was in no case employed) were then introduced, but a pressure from outside was maintained during the whole experiment. At the conclusion of

the experiment, the mixed gases were pumped out, passing through the acidified asbestos to absorb any ammonia, and over heated copper to absorb the oxygen; it was then washed out with carbonic anhydride until the recovered gas was pure carbonic anhydride.

As regards the indirect method, the nitrogen of the seeds was determined by Kjeldahl's method, that of the soil by Dumas' method as modified by Schloesing, sen. (*Compt. rend.*, **107**, 296), 200—250 grams of sand or soil being used for each analysis. At the conclusion of the experiments, the soil from each pot was heated in a flask at 70°, and the vapour given off condensed in a tube surrounded by ice. This water was collected and the ammonia determined. The total nitrogen was then determined in the soil.

In the 1890 experiments in which peas were grown in sand (containing 0·000186 per cent. of nitrogen) with minerals, pots 1 and 2 were microbe-seeded, pot 3 not seeded and left open to the air. The plants of 1 and 2 grew to the height of about 20 cm. and flowered, but did not produce seeds; there was much development of roots, with many nodules. The plants of pot 3 grew to a height of 31 cm., but were slender and without branches; there were pods, but no completely developed seeds. The roots had no nodules. The following table shows the amount of dry produce and the approximate amount of carbonic anhydride assimilated:—

	Dry matter, grams.	CO_2, litre.
Pot 1	2·55	1·4
,, 2	2·10	1·3
,, 3	1·83	—

The nitrogen results are given below, together with those of the subsequent experiments.

In 1891, a poor subsoil containing 0·008722 per cent. of nitrogen was employed (2·5 kilos., pots 1—7; 2·0 kilos., pots 8—13), with the addition of chalk (5 grams), a mixture of several rich soils (5 grams), and a nutritive solution containing, among other things, a little nitrate. The first series comprised the following:—1. Jerusalem artichoke. 2. Oats. 3. Peas. 4. Tobacco. 5, 6, 7. Check experiments. The results were as follows:—1. No flowers, fresh weight about 17 grams, about 2 litres of carbonic anhydride assimilated. 2. Fresh weight (three plants) 25 grams, height 49 cm., 6 litres of CO_2 absorbed. 3. Flowers formed, height 49 cm., many nodules on roots, 4 litres of CO_2 absorbed. 4. 9—10 cm. high, 4 litres of CO_2 assimilated. The surface of the soils in pots 1—5 was covered with lower green vegetation consisting of mosses (*Bryum* and *Leptobryum*) and algæ (*Conferva*, *Oscillaria*, and *Nitzschia*). The soils of pots 6 and 7 were practically free from visible growth of any kind. The nitrogen results given in the table (p. 1023) show that nitrogen fixation took place in pots 1—4, with higher and lower vegetation, and in pot 5, with lower vegetation, but not in pots 6 and 7, where there was no vegetation. Moreover, with regard to pot 5, it was found that only the upper layer of soil (weighing 56·8 grams, and including about 1 gram of dry vegetable matter) had gained nitrogen,

	Direct method.			Indirect method.				
	Nitrogen.			Nitrogen.				
				At commencement.		At conclusion.		Gain.
	Supplied, c.c.	At conclusion, c.c.	Fixed, mgm.	Soil,* mgm.	Seed, mgm.	Soil,† mgm.	Produce, mgm.	Mgm.
Experiments made in 1890. *Sand.*								
1. Peas‡	2681·2	2652·1	36·5	4·3	28·3	15·1	58·1	40·6
2. „	2483·3	2457·5	32·4	4·3	28·2	17·5	49·1	34·1
3. „ §	—	—	—	4·3	28·2	8·3	24·8	0·6
Experiments made in 1891. *Soil.*								
1. Jerusalem artichoke	2935·1	2927·8	9·2	268·18	10·13	240·32	46·31	8·3
2. Oats	2660·3	2629·7	38·5	242·98	2·82	247·73	33·47	35·4
3. Peas	2955·7	2881·7	93·3	242·98	40·24	262·40	121·89	101·1
4. Tobacco	3241·8	3222·7	24·0	242·98	0·0	243·56	26·02	26·6
5. Check	3203·1	3192·1	13·9	242·98	0·0	235·64	22·12	14·8
6. Check	901·9	903·4	—	—	—	—	—	—
7. Check	825·9	851·6	—	—	—	—	—	—
8. Check	3101·3	3110·5	1·0	190·60	0·0	194·59	0·0	4·0
9. Barley	3023·9	3023·9	0·0	190·60	3·05	177·08	18·38	1·8
10. Peas	3103·3	2996·2	134·6	190·47	32·76	195·15	170·54	142·4
11. Mustard	3503·1	3505·2	−2·6	190·48	3·98	179·66	17·31	−2·5
12. Cress	3485·7	3488·7	−3·8	204·47	1·92	179·79	28·65	2·0
13. Giant spurrey	3477·5	3479·4	−2·4	204·47	0·49	198·00	10·16	3·2

* Including (in 1891 experiments) nitrogen as nitrate added; 37·7 mgm., pot 1; 12·5 mgm., pots 2—5; 14·0 mgm., pots 12 and 13.
† Including (in 1891 experiments) traces of nitrogen as ammonia found in the asbestos tube and in the water distilled from the soil.
‡ Pots 1 and 2, microbe seeded. § Left open to the air and not infected.

the percentage of nitrogen of the rest of the soil remaining practically the same. In connection with this point, Frank (*Landw. Jahrb.*, 1888) already admitted that such a gain could be brought about, but without sufficient evidence. Gautier and Drouin also found that algæ enrich soil in nitrogen, but attributed it to the absorption of combined nitrogen.

In order to avoid the growth of lower vegetation in the next experiments, a layer of dry sand was put over the surface of the soil. The experiments were: Pot 8, check; 9, barley; 10, peas; 11, white mustard; 12, cress; and 13, giant spurrey. The barley grew to a height of 50 cm., and assimilated 2·6 litres of carbonic acid. The peas produced several flowers, grew to a height of 64 cm., decomposed 3·7 litres of carbonic anhydride, and had many nodules on the roots. The mustard grew to 55 cm., and decomposed 2·2 litres of carbonic anhydride. The cress grew to a height of 65 cm., decomposed 3 litres of carbonic anhydride, and produced numerous flowers. The spurrey remained small, 6 cm.

The table, p. 1023, summarises the whole of the results as far as nitrogen is concerned, obtained by two methods, direct and indirect.

The chief points of interest furnished by the authors' experiments are the confirmation, by a direct method, in conjunction with the indirect method, (1) that the *Leguminosæ*, or at least peas, have the power of fixing elementary nitrogen, (2) that some of the lower green plants have the same power, (3) that soils free from visible growth did not fix nitrogen, and (4) that barley, mustard, cress, and spurrey did not fix nitrogen when, under the same conditions, peas did. N. H. M.

Composition and Cultivation of the Jerusalem Artichoke. By G. Lechartier (*Ann. Agron.*, **18**, 68—91).—Experimental plots of this crop have been grown at the agricultural station of Rennes for the six years 1885–90. No nitrogenous manure was used. Plot 1 received no manure; Plot 2, superphosphate equal to 100 kilos. P_2O_5 per hectare; Plot 3, potassium chloride equal to 175 kilos. K_2O per hectare; Plot 4, the same quantities of superphosphate and potassium chloride, mixed. The crop in 1889 was a failure. The yields of the other years are summarised below :—

Tubers. Kilos. per hectare.	1885.	1886.	1887.	1888.	1890.	Mean.
1. No manure	20243	19987	10206	8180	12947	14312
2. Superphosphate only.....	21600	18730	8978	6600	11886	13559
3. Potassium chloride only....	35371	27620	24700	23680	21168	26508
4. Mixture of the two	36606	33385	24008	22890	19000	27978

This soil contained nitrogen, 0·170—0·122; P_2O_5, 0·096; CaO, 0·229—0·193; MgO, 0·405—0·283; and K_2O, 0·309—0·337 per cent.

The extreme dependence of the yield of tubers on the supply of

assimilable potash in the manure, even when the soil is not poor in total potash, is clearly shown in the above figures. The author has followed the variations in the proportions of mineral ingredients in stem, leaf, and tuber, in the different years, on the crops of the differently manured plots, and at different stages of development, by means of very elaborate analyses. The mean composition of the ash of the crop on the best manured plot (Plot 4) was as follows:—

	Per cent. of dry matter in		
	Stems.	Leaves.	Tubers.
Ash	2·860	—	4·193
SiO_2	0·220	4·741	0·299
P_2O_5	0·113	0·326	0·588
CaO	0·920	5 537	0·207
MgO	0·497	1·817	0·139
K_2O	0·330	0·209	2·162
Na_2O	0·052	—	0·100

The figures above represent the distribution of mineral matter at harvest in November or December, the stems being nearly dry, and the leaves black and withered. The maxima and minima of the two principal ingredients were:—

	Tubers.		Leaves.		Stems.	
	Max.	Min.	Max.	Min.	Max.	Min.
P_2O_5	0 740	0·320	0·658	0·200	0·264	0·071
K_2O	2·470	1·640	0·370	0·127	0·584	0·075

The minimum of potash found in the tubers probably corresponds with the smallest quantity necessary to normal development. In wet seasons, the proportion of potash and phosphoric anhydride in the tubers is much higher than in dry seasons. The leaves in wet seasons from the unmanured plots contained less potash than in dry, because they were drained to a greater extent by the greater development of tubers. The influence of the different manures is greatest on the composition of the leaves because the tubers develop normally, so far as they can, at the expense of the leaves. Phosphatic manure applied alone increased neither the phosphoric acid nor the potash assimilated; but potash manure applied alone doubled the quantity of phosphoric acid assimilated, besides trebling or quintupling the amount of potash assimilated. Tubers lifted in September are richer in phosphoric acid and potash than those lifted in November or December, part of the

food at first absorbed being probably used in the growth of the tubers or the development of new ones.

Analysis of the leaves in three stages of development—young and green, yellow and beginning to wither, old and black—from crops on the differently manured plots and in the different years, brings out the following facts:—The green leaves contain twice or even four times as much potash when potash manures are supplied; magnesia is in larger proportion when no potash manure is given; lime is in far less proportion in the young than in the old leaves; phosphoric acid is in much greater proportion in the young leaves on all the plots (17—22 per cent.) than in the yellow leaves (7—14 per cent.) or the blackened leaves (4—12 per cent.). In the yellow leaves, the proportion of potash falls to 1·8—2·4 per cent. on the plots receiving no potash manure; whereas, on those receiving potash manure, it is as high (11—50 per cent.) as in the young leaves.

In the blackened leaves, where no potash was given in manure, the potash fell to 0·6—0·7 per cent.; where it was supplied in manure, there was still 15 per cent. The change from yellow to green of the leaves is not caused by drying, both containing 70—80 per cent. water, but by lack of P_2O_5 or K_2O. These materials being withdrawn from the leaves at first formed for tuber formation later on, eventually fall below certain limits (3·48—4·10 per cent. for P_2O_5 and 3·18—3·36 per cent. for K_2O), and when this is the case, these leaves commenced to turn yellow and afterwards black. On the unmanured plots, many leaves undergo these changes early in the autumn, if the soil is deficient in P_2O_5 or K_2O; when phosphatic and potash manures are supplied, many more leaves remain green until late in the season. Phosphate alone being supplied in the manure, the blackened leaves contained P_2O_5 6·98 and K_2O 1·17 per cent.; potash alone being supplied, they contained P_2O_5 1·07 and K_2O 15·64 per cent.

The author proposes to make comparative estimations of P_2O_5 and K_2O in the old and young leaves taken simultaneously from a growing plant, in order to find out which of these two substances is lacking (in assimilable condition) in the soil; for some crops (? most) a similar proceeding would show the presence or absence of sufficient assimilable nitrogen. The richness of a leaf in mineral matter varies greatly with the season, the soil, the manures supplied, the stage of vegetation, and with its position on the stem; these variations are much greater than are found in tuber or in seed. J. M. H. M.

Kaolin in Arable Soil. By R. Sachsse and A. Becker (*Landw. Versuchs-Stat.*, **40**, 245—255).—Kaolin, when heated in a platinum crucible so as just to give out light, lost 11·04—11·91 and in one case 10·98 per cent. of water; when heated by placing the crucible in melted saltpetre for two hours, the loss was 10·69 per cent. The silicate so produced had the sp. gr. 2·461, and was decomposed by evaporating down with dilute hydrochloric acid. The residue, insoluble in acid and in potash, amounted to 11·30—11·90 in the case of the first mentioned (which lost 11·04—11·91 per cent. of water) and 18·6 and 23·48 per cent. where the loss of water had been respectively 10·98 and 10·69 per cent.

Myelin (containing H_2O, 14·27; SiO_2, 45·41; and Al_2O_3, 40·48 per cent.), when gently ignited, lost 13·0—13·9 per cent. of water, and left a residue, insoluble in acid and alkali, only amounting to 2·4 per cent.

Nacrite (of the composition H_2O = 15·65, SiO_2 = 44·15, and Al_2O_3 = 40·85 per cent.), which is said to be entirely soluble in hydrochloric acid, was found to be soluble only to the extent of about 50 per cent. After ignition, it dissolved, all except 1·43 per cent.

The above results with kaolin agree better with the molecular relation $5Al_2O_3 : 9SiO_2$ than with $Al_2O_3 : SiO_2$.

When the silicate (sp. gr. 2·461) is digested with aqueous sodium silicate (potassium silicate is almost without action) for an hour, a gelatinous substance of the following composition is obtained:—

	SiO_2.	Al_2O_3.	Na_2O.	H_2O.
1	52·72	25·93	12·21	8·88
2	53·01	27·51	11·20	8·66

It has thus taken up water as well as sodium silicate, and become converted into a kind of analcime.

Kaolin was estimated in two muds from arable soil. This was done by extracting the soil, previously dried at 100°, with dilute hydrochloric acid, and estimating the dissolved sesquioxide, and the silica soluble in potash. These determinations were again made in second samples which had been gently ignited, and the *minus* of residue insoluble in acid and potash, or the *plus* of silica and sesquioxide, which was obtained in the second experiment as against the first, calculated as kaolin. The composition of the muds, the one from a heavy clay and the other from a red soil from Paraguay, is given, as well as that of the finest mud of the three loams previously analysed by the authors (compare *Landw. Veruchs-Stat.*, **38**, 411).

N. H. M.

Analytical Chemistry.

Improvements in Burettes. By A. F. Reid (*Chem. News*, **65**, 125).—A metal scale constructed to slide on the outside of an ordinary burette, or a graduated tube fixed firmly in an india-rubber ring, which slides up and down, as a piston, inside the burette, is suggested as useful for measuring the delivery of successive small quantities of solution from the same burette. D. A. L.

Use of Iodic and Bromic Acids in Quantitative Analysis. By A. Schwicker (*Chem. Zeit.*, **15**, 845—846).—The author's process agrees in principle with the one described by Feit and Kubierschky (compare this vol., p. 910), but is carried out in a somewhat different manner. The process will prove of good service when the solutions are very dilute, and completely oxidisable by bromic acid in the cold, and it dispenses with the boiling off of the liberated bromine.

Iodic acid is a slow oxidant, and scarcely useful except for the estimation of sulphurous acid; but bromic acid is a useful oxidant, even in a strongly diluted state. The oxidising action of iodic, or bromic, acid may be represented by the equation $2HIO_3 = H_2O + I_2 + O_5$. 2 mols. of iodic, or bromic acid, which, if brought into contact with potassium iodide, would have liberated 6 mols. of iodine according to the equation $2HIO_3 + 10HI = 6H_2O + 6I_2$, give, after reduction, only 1 mol. of iodine. The diminution in iodine corresponds with the oxygen of the iodic or bromic acid which has been taken up by the substance under examination. If now the amount of iodine liberated by potassium iodide is estimated by sodium thiosulphate, before and after the action of the reducing agent, the amount of the latter may be readily calculated.

It is not necessary, of course, to use either bromic or iodic acid in the pure state, but a solution of the readily obtainable potassium iodate or bromate, mixed with sulphuric acid, may be used. The test analyses practised on sulphurous acid and sodium sulphite, also on nitrites of known strength, are very satisfactory. L. DE K.

Separation of Iodine, Bromine, and Chlorine. By C. SCHIERHOLZ (*Monatsh.*, **13**, 1—39; compare Field, this Journal, 1857, 234, and *J. pr. Chem.*, **73**).—When each of the three halogens is present in fair quantity, the author adopts an indirect method, in which two weighings only are necessary. Two equal volumes of the neutral solutions, in which the halogens are to be determined, are measured out, and one of them is accurately titrated with a 1/20 normal silver nitrate solution. The number of c.c. required, *a*, and the weight of the silver precipitate, *b*, are accurately determined. The second portion of the solution is treated with a few grams of potassium bromide, and the same volume of the silver nitrate solution as was required to precipitate the halogens in the first portion, is added. The solution is boiled for some time, diluted with water, and the weight, *c*, of the resulting precipitate, which contains all the iodine, all the silver, and some bromine, is noted. By means of the three values *a*, *b*, and *c*, the quantity of each halogen present can be readily calculated.

If only a small quantity of iodine and bromine is present with relatively much chlorine, the method of estimation depends on the facts that silver iodide is insoluble in moderately concentrated solutions of sodium chloride, and that bromine and chlorine can be separated by distillation with solutions of potassium permanganate and aluminium sulphate (compare White, Abstr., 1888, 1130). For the latter process, the author employs a distillation apparatus, consisting of a retort and condenser, and made of glass in one piece, the last portions of the bromine being expelled by boiling with a little dilute sulphuric acid. The bromine is absorbed in a flask containing dilute ammonia, whereby it is converted into ammonium bromide and probably partly into ammonium hypobromite; the whole of the bromine is, however, precipitated as silver bromide, on adding silver nitrate to the solution. This method of separating the iodine is only available when (say, in a mixture of sodium salts) it is

present in the proportion of not more than 1 part of iodide to 6 or 7 of bromide and 1000 of chloride, under which circumstances, on the addition of a little silver nitrate, only silver iodide is precipitated, since silver bromide and silver chloride are soluble in strong sodium chloride solution. If, however, more bromide, or more iodide and bromide, are present than is indicated by the above-given ratio, it is best to precipitate and estimate the iodide as palladium iodide.

In making the above separations, the author has incidentally investigated the solubility of silver chloride, bromide, and iodide in solutions of the halogen salts of the alkalis, more particularly in sodium chloride. Such solutions dissolve 4—5 times as much of the halogen salts of silver at their boiling point, as at the ordinary temperature. The concentration of the solution of the halogen salts of the alkalis has also a marked effect on the solubility of the silver compounds; a 10 per cent. solution of sodium chloride and 1 per cent. solution of potassium iodide dissolving scarcely any recognisable quantity of the corresponding silver compounds. The very great difference between chlorine and iodine is shown both in the relative solubility of silver chloride and silver iodide, and in the different solvent power of the halogen alkali salts on silver nitrate, silver chloride, &c.; bromine occupying a position between chlorine and iodine. For example, 100 grams of sodium chloride or of potassium chloride in a 20 per cent. solution dissolves hardly a trace of silver iodide, whilst 100 grams of potassium iodide in concentrated solution dissolves about 90 grams of the salt, and a boiling saturated solution dissolves 4—5 times that quantity. Mixtures of the halogen salts of the alkalis, in particular proportions, are unable to dissolve as much of the silver salt as each can before admixture. G. T. M.

Analysis of Sodium Nitrite. By G. Lunge (*Chem. News*, **65**, 134).—According to the author, both the aniline and sulphanilic acid methods (compare this vol., p. 751) were in use 14 years ago, but are tedious, troublesome, and misleading, whereas his own modification of the permanganate method is rapid, simple, and accurate.

D. A. L.

Estimation of Phosphoric Acid in Fertilisers containing Cotton-seed Meal. By F. B. Dancy (*Chem. News*, **65**, 162—163, 170—172).—The author shows that the method of dissolving in nitric acid with a small quantity of hydrochloric acid and precipitating by molybdate is not applicable for determining phosphoric acid in fertilisers containing cotton-seed meal, inasmuch as, although they dissolve readily enough, the solutions do not give up their phosphoric acid to molybdate, and, therefore, low results are obtained. Moreover, solution in hydrochloric acid and potassium chlorate has proved, in some instances, inadequate for the purpose. Fusion with equal parts of sodium carbonate and potassium nitrate gives maximum results, but takes too long, whilst incineration and subsequent solution of the ash in nitric acid sometimes gives low results, owing to the ignited phosphate not being completely soluble in that solvent; this difficulty is apparently overcome by dissolving the ignited residue

in hydrochloric acid, in which it is readily and wholly soluble. This, therefore, furnishes a satisfactory basis for a desirable method.

D. A. L.

Testing Metallic Iron for Arsenic. By O. Sautermeister (*Chem. Zeit.*, **15**, 1021—1022).—The author, applying the official test of the German Pharmacopœia, could get no reaction for arsenic even when 0·1 gram of arsenic trioxide was purposely added. The test consists in dissolving 1 gram of the metal in dilute hydrochloric acid, in a Marsh's apparatus, and allowing the hydrogen flame to play upon a porcelain dish. An examination of the insoluble residue revealed, however, the presence of arsenic, which had been reduced to the metallic state. This fact was, indeed, known to Wöhler in 1839, but has since been overlooked.

The test is, however, more satisfactory when about 2·5 grams of zinc is added to the iron. Although the arsenic does not show at first, it will be gradually evolved when the hydrogen comes off briskly. 0·1 per cent. of arsenic in a sample of iron may be detected in this manner.

L. de K.

Wiborgh's Gasometric Method for the Estimation of Carbon in Iron. By H. v. Jüptner (*Chem. Centr.*, 1892, i, 237; from *Osterrungar. Zeit. Berg. Hütt.*, **39**, 533—537).—The author recommends several slight alterations in the method of using the apparatus.

J. W. L.

Estimation of Gold, Tin, and Cadmium in Alloys. By W. French (*Chem. News*, **65**, 133—134).—The following method is recommended as expeditious and trustworthy. 1 or 2 grams of alloy is heated with just sufficient hydrochloric acid to dissolve the tin and cadmium, and the gold is collected and weighed; the filtrate is then nearly neutralised with potassium hydroxide, 4 to 5 c.c. of hydrogen peroxide (10 vols.) added, the whole diluted to about half a litre, and heated to boiling. In this way the tin is precipitated in a convenient form, and is washed, dried, ignited, and weighed as stannic oxide. The solution is evaporated to about half its bulk, and the cadmium is precipitated at the boiling point by means of potassium carbonate.

D. A. L.

Estimation of Manganese in Iron and Steel. By H. Rubricus (*Chem. Zeit.*, **15**, 882).—The author remarks that he has never had any trouble in determining the end point when titrating manganese with permanganate, and recommends the following process:—

10 grams of the iron or steel is dissolved in 50 c.c. of hydrochloric acid (sp. gr. 1·15), the solution filtered into a 500 c.c. flask, and made up to the mark. 100 c.c. of the liquid (= 2 grams of the sample) is oxidised with nitric acid, cooled, diluted to 600 c.c., and nearly neutralised with sodium carbonate. The iron is now precipitated with a very moderate excess of elutriated zinc oxide; 2 grams of magnesium sulphate is added, and the liquid heated to boiling. On adding the permanganate, the clear, supernatant liquid first becomes brownish, but then gradually clearer until at last the pink colour of the permanganate becomes quite distinct. On account of the great

dilution of the liquid, 0·1 c.c. of permanganate solution must be allowed for. L. DE K.

Analytical Application of Barium and Hydrogen Peroxides. By E. DONATH (*Chem. Zeit.*, **15**, 1085—1086).—The author's process of oxidising chrome-iron ore by means of barium peroxide has been tried by Kinnicut and Patterson, who failed, however, to get satisfactory results. These chemists, therefore, recommend the addition of sodium carbonate. The author again asserts that the ore is completely attacked by barium peroxide alone, provided this is of good quality. The probable reason why Kinnicut and Patterson's results were not satisfactory is that their chrome-iron ores were of exceptional richness and their barium peroxide of poor quality. The author has never insisted on performing the oxidation in a porcelain crucible, but merely remarked that such a crucible may be used.

When sodium carbonate is added, the mass fuses, and is therefore not so easily removed from the crucible; moreover, the use of an alkali causes a portion of the chromium to remain as oxide, which has to be oxidised to chromate by hydrogen peroxide. The usual method of estimating the chromic acid by reduction with a ferrous salt, and estimation of the excess of the latter by permanganate, is, in the author's opinion, inferior to the plan of estimating it by means of potassium iodide and sodium thiosulphate.

As regards hydrogen peroxide, this is an excellent oxidant for ferrous salts, and its excess is very readily removed by boiling. It rapidly oxidises ammonium sulphide without separation of sulphur, and may be successfully used to oxidise an ammoniacal solution of arsenic trisulphide before precipitation with magnesia mixture.

L. DE K.

Estimation of Kaolin in Arable Soils. By R. SACHSSE and A. BECKER (*Landw. Versuchs-Stat.*, **40**, 245—255).—See this vol., p. 1026.

Röse's Process for the Estimation of Alcohol. By L. GRÜNHUT (*Chem. Zeit.*, **15**, 847—848).—A few years ago, Röse proposed a new process for the direct estimation of alcohol. A small quantity of the sample is largely diluted with water, mixed with a large excess of potassium permanganate, and then suddenly mixed with an excess of strong sulphuric acid. After a few minutes, the alcohol is supposed to be completely oxidised to carbonic anhydride and water. The excess of permanganate is destroyed by the addition of a known quantity of potassium tetroxalate, the excess of which is then in turn estimated by permanganate. Röse's preliminary experiments were very satisfactory.

The author has, however, found, as Benedikt did previously, that the reaction does not proceed regularly on these lines, and that a good deal depends on the amount of sulphuric acid, which, if added in insufficient quantity, causes a very incomplete oxidation. If, on the other hand, too much acid is added, an independent decomposition of the permanganate will set in and the result will be untrustworthy.

The process cannot, therefore, be recommended for the estimation of alcohol in technical products. L. DE K.

Action of Alkaline Mercuric Cyanide on Maltose, Dextrose, and Dextrin. By J. A. WILSON (*Chem. News*, **65**, 169).—Alkaline mercuric cyanide has been said to destroy the optical activity of dextroglucose and maltose, but to leave dextrin unchanged. The author has put this to the test:—10 c.c. each of solutions of these carbohydrates (= 1 gram of the dry substance) were boiled severally for two minutes with a slight excess of a solution of alkaline mercuric cyanide, containing 12 grams of mercuric cyanide and 12 grams of sodium hydroxide in 100 c.c. of water. The cooled solutions were acidified with hydrochloric acid, diluted to 50 c.c., clarified by animal charcoal, and polarised in a 200 mm. tube. The results show that the optical activity of dextrose is entirely destroyed by this treatment, that of maltose diminished from +26 to +9, and that of dextrin from +37·2 to +33·5; the dextrin was not quite pure, but not sufficiently impure to account for this loss. D. A. L.

New Reagent for Acetone. By A. SCHWICKER (*Chem. Zeit.*, **15**, 914).—A mixture of acetone and aqueous ammonia dissolves powdered iodine and gets warm. The liquid becomes turbid, and after some time deposits iodoform. At the same time, a substance is formed which is probably an iodine substitution product of acetone, and which is characterised not only by a pungent smell, but also by exciting a flow of tears. There is no apparent evolution of any gas, but a little acetic acid is formed. The process, which is not affected by the presence of alcohol, is carried out as follows:—

The solution, which must be free from aldehyde, is mixed with a few drops of ammonia and a few drops of N/10 iodine solution. Nitrogen iodide is formed at first, but disappears on shaking and warming. If acetone is present in not too small quantity, the iodoform reaction makes its appearance at this point, and is improved by the addition of a little more iodine. The characteristic odour is not greatly obscured by the ammonia. If the nitrogen iodide refuses to disappear, it may be readily removed by the cautious addition of a few drops of a very weak solution of sodium thiosulphate.

If traces only of acetone are present, the reaction will still make its appearance if a little more time be given. The test may be applied to detect acetone in urine. L. DE K.

Estimation of Uric Acid. By H. C. GEELMUYDEN (*Zeit. anal. Chem.*, **31**, 158—180).—An accurate process for estimating uric acid in urine is still a desideratum. Salkowski's method of precipitation with ammoniacal silver and magnesium solution is open to the objection that other nitrogenous substances, especially xanthine and its congeners, are precipitated with the uric acid. The necessity for applying a correction for the solubility of uric acid in the final wash water is a further objection (see also Abstr., 1889, 1250). Ludwig's modification (Abstr., 1886, 102) is no improvement, and introduces fresh sources of error. The author has sought to employ the precipitation of uric acid by barium chloride as a means of estimation, and

has obtained promising results, but is obliged to discontinue the investigation without bringing the method to perfection. Instead of weighing the precipitate, it is preferable to determine the nitrogen in it by Kjeldahl's method. From a solution of sodium hydrogen urate, the uric acid can be almost absolutely precipitated by adding barium chloride, heating for half an hour on the water-bath, allowing the mixture to remain until next day, and filtering off. Solutions containing as little as 9 milligrams in 100 c.c. give very satisfactory results. The presence of ammonium chloride or of disodium hydrogen phosphate or of the two together, is without influence, but free acid or free alkali, and the latter especially in presence of phosphates, prevents complete precipitation. The acidity of normal urine has a similar effect, so that neutralisation is requisite, but this in the presence of phosphates presents peculiar difficulties. If, however, the addition of alkali is stopped, either when precipitation of earthy phosphates commences, or when litmus paper wetted with the liquid just remains blue after drying, precipitation of the uric acid seems to be complete, but other nitrogenous substances appear to be thrown down, since the results calculated from the nitrogen found come out higher than by Salkowski's method. The excess is the greater, the richer the urine is in uric acid, and in one case amounted to 70 per cent. On the other hand, the uric acid obtainable from the barium precipitate (in a case where the barium method showed 0·0059 gram, or 13 per cent. more than Salkowski's) was 0·00365 gram, or 8 per cent. less than Salkowski's; neither could it be ascertained that more than traces was lost. Dilution of the urine leads to lower, but apparently untrustworthy results, since a degree of dilution which would not interfere with a satisfactory estimation if using a pure urate, yet when applied to urine, reduces the amount of nitrogenous substance precipitated to a small fraction of that shown by Salkowski's method. The subject needs and seems to deserve further investigation. M. J. S.

Estimation of Cream of Tartar in Wine Lees. By B. Balli (*Chem. Zeit.*, **15**, 989—991).—The author recommends a process which may at first sight seem rather too complicated for commercial purposes, but which will be found of great use to makers of cream of tartar, as it will enable them to calculate the exact amount of hydrochloric acid to be added in case the wine yeast has been fermenting, and so partly changed into normal potassium tartrate or, as may also happen, into a mixture of potassium hydrogen tartrate and potassium carbonate.

The process may be briefly described as follows:—It consists of two separate analyses. 1. The analysis proper. The cream of tartar is extracted by boiling water and so exposed to the action of the carbonates. The portion acted on by the potassium carbonate is completely changed into normal tartrate, whilst that acted on by calcium carbonate is to the extent of one half changed into normal tartrate. By neutralisation with potash or soda, the remaining, permanent cream of tartar is also made into a soluble normal tartrate, which may then be estimated as potassium hydrogen tartrate by the addition of acetic acid. The result will be, *constant* cream of tartar

+ ½ loss caused by the calcium carbonate + total loss caused by potassium carbonate. 2. The check analysis. The object is the estimation of the amount of pre-existing, or subsequently formed, potassium normal tartrate, also the loss caused by the carbonates. The cream of tartar is dissolved in boiling water, and is, of course, acted on by the carbonates. On cooling, the *constant* cream of tartar practically crystallises out, and the mother liquor retains normal potassium tartrate, which may be precipitated as the acid salt by the addition of acetic acid. The result will show, ½ the loss caused by the calcium carbonate + the loss caused by the potassium carbonate. The difference between the chief and the check analyses gives the constant bitartrate, or, plainly put, the amount of cream of tartar obtained by a single crystallisation. L. DE K.

Detection of Margarin in Butter. By H. RODEWALD (*Landw. Versuchs-Stat.*, **40**, 265—275).—Butter and margarin differ only in their quantitative composition, their qualitative reactions, volatile and insoluble fatty acids, combination with iodine, and refractive property being common to both. The usual process consists in comparing the numbers obtained with the minimum and maximum numbers of natural butter. The method is uncertain when the results fall beyond these numbers, inasmuch as other minimum and maximum numbers may be found for natural butter. More difficult cases occur when the results given by a sample (known to be probably adulterated) fall within the numbers obtained with pure butter. The object of the present paper is to indicate how, in such cases, the probability of adulteration may be established arithmetically from all the results. The numbers obtained by Schrodt and Henzold with pure butter are employed.

In the case of large additions of margarin, the estimation of insoluble fatty acids gives the most certain results. The methods next in value are the estimation of volatile acids and the refractive exponent.

The worst kind of adulteration is, when all the butter is mixed with a little magarin (10—15 per cent.), but butter so adulterated would always be liable to suspicion. N. H. M.

Analysis of Beeswax. By C. MANGOLD (*Chem. Zeit.*, **15**, 799—800).—Owing to the great fluctuation of the acidity, saponification, and iodine numbers of genuine yellow beeswax, adulteration with less than 6 per cent. of paraffin or ceresin is almost beyond detection. A process has been worked out by A. and P. Buisine, which the author thought was well worth trying. It is based on the decomposition of wax soap by hot potash-lime, which does not act on the paraffins, but decomposes the fatty matter with elimination of hydrogen, which serves as a measure of their amount. The paraffins may be extracted from the residue.

The author's investigations practically confirm those of Buisine, but he now recommends the following process:—2 to 10 grams of the wax is saponified by melting it with powdered potash-lime, the reaction being aided by stirring with a glass rod. After complete cooling, the soap is powdered, and intimately mixed with three times its

weight of potash-lime, and the powder transferred to a thick-walled, pear-shaped bulb-tube, which is heated for three hours at 250° in a mercury bath contained in an iron vessel. This is provided with a lid, which screws on air-tight, and is pierced with four apertures through which pass air-tight, respectively, the pear-shaped bulb, a thermometer, a thermostat, and a long tube open at both ends to condense any mercury vapour. A tube connects the pear-shaped bulb with a Hofmann's burette, in which the hydrogen is measured.

The author's process is, however, more particularly directed to the estimation of the paraffins. After three hours, when no more gas will be given off, the residue is powdered, and to prevent any loss the bulb-tube is also broken up, and the whole is extracted with light petroleum in a Soxhlet's apparatus. The petroleum is distilled off, and the residual paraffin dried at 110° and weighed. On applying the process to yellow beeswax of undoubtedly genuine origin, the amount of natural hydrocarbons was found to vary from 11·02 to 14·7 per cent., although in practice the average amount may be put down as 13·5 per cent.

A sample of Transylvanian wax, tested by the author, had an acidity equivalent of 16·66, and a true saponification number of 56·02, which pointed to adulteration with paraffin, or a similar substance. Analysed by the author's method, the percentage of hydrocarbons came, indeed, to 28·12, corresponding with 17 per cent. of adulteration, calculated on the original sample. A sample of wax, which had been purposely adulterated with 8 per cent. of paraffin, showed on analysis 7·4 per cent.

The amount of hydrocarbons in samples of white wax varied from 10·93 to 15·48 per cent., but the purity of some of the samples was rather doubtful. L. DE K.

Estimation of Oil of Mustard. By A. SCHLICHT (*Zeit. anal. Chem.*, **30**, 661—665).—In the course of a study of the decomposition of potassium myronate, a method of estimating allylthiocarbimide in presence of water became necessary. Foerster's method, which consists in converting the compound by ammonia into thiosinamine, and this into sinamine and mercuric sulphide by boiling with mercuric oxide, gives low results. So also does the method of Dircks (Abstr., 1883, 245), which moreover requires much time. The following modification is, however, both simple and trustworthy. The mustard oil is shaken for some time in a corked flask with a mixture of 20 parts of potassium permanganate and 5 parts of potassium hydroxide (both of which must be free from sulphates), and the mixture is finally heated nearly to boiling. The whole of the sulphur is thus oxidised to sulphuric acid. After slight cooling, 5 c.c. of alcohol is added for every gram of permanganate used. This completes the precipitation of the manganese present. The mixture is completely cooled, largely diluted, made up to a known volume, and filtered. A measured portion of the filtrate is slightly acidified with hydrochloric acid, and treated with a solution of iodine in potassium iodide until a feeble yellow colour remains even after warming. This reproduces any sulphuric acid which has been

reduced by the aldehyde, and also removes the aldehyde itself. The sulphuric acid is now determined by barium, and the weight of barium sulphate multiplied by 0·42492 gives the amount of mustard oil. Test analyses gave results varying from 99·74 to 99·95 per cent.

M. J. S.

Picric Acid as a Test for Guanidine. By O. Prelinger (*Monatsh.*, **13**, 97—100).—See this vol., p. 950.

Specific Gravity of Fibres. By De Chardonnet (*Compt. rend.*, **114**, 489).—The values for the specific gravity of fibres as determined by Vignon's method (this vol., pp. 254, 645) are too low, as the air is not completely expelled from their interstices.

A more trustworthy method consists in mixing the silk, cut into pieces not more than 1 mm. long, with a solution of cadmium borotungstate of about the same specific gravity, and exposing the mixture to a vacuum and atmospheric pressure alternately for some hours, to ensure that the fibres are completely permeated with the liquid. Water or concentrated solution of the above salt is then cautiously added until the cloud of fibres remains permanently suspended in the liquid. The specific gravity of the liquid and solid must then be equal, and hence by taking the specific gravity of the filtered liquid, the required figure is obtained.

The values thus obtained for raw and refined silk are 1·66 and 1·43 respectively.

Jn. W.

Specific Gravity of Silk. By L. Vignon (*Compt. rend.*, **114**, 603—605).—A reply to de Chardonnet. The author finds that exposure to reduced pressure under benzene for 10 minutes removes all the gas, and no alteration in sp. gr. is produced by exposure to reduced pressure for three days. The higher results obtained by de Chardonnet are due partly to the mechanical treatment to which the silk was subjected, and partly to the use of strong solutions of metallic salts for the determination of the sp. gr. The author finds by direct experiment that the silk absorbs saline matter from these solutions.

C. H. B.

Colour Reactions of the Proteïd Precipitate produced by Potassium Ferrocyanide. By H. Winternitz (*Zeit. physiol. Chem.*, **16**, 439—444; compare Abstr., 1891, 1130).—The precipitate produced in a proteïd solution by the addition of potassium ferrocyanide is a very delicate reaction; it is given by a solution containing only 1 part of the proteïd in 50,000. It is not, however, an absolute proof of the existence of proteïd in such investigations, for instance, as the question of the presence of proteïd in normal urine. It is then necessary to test the precipitate by means of the various colour reactions for proteïds. Of these, that given by Millon's reagent is the most delicate. The precipitate also gives the Adamkiewicz reaction, the xanthoproteïc reaction, Liebermann's reaction, and the reaction of Max Schultze (with concentrated sulphuric acid and a drop of dilute cane-sugar solution). It does not give Fröhde's reaction (blue colour with sulphuric acid containing molybdic acid, *Annalen*, **145**, 376).

W. D. H.

General and Physical Chemistry.

Colours and Absorption-spectra of Thin Metallic Films and of Incandescent Vapours of the Metals: Electrical Volatility. By W. L. Dudley (*Amer. Chem. J.*, **14**, 185—190.)—The author describes a number of methods he has employed in the preparation of thin metallic films, and gives a table comparing the colour of metals by transmitted light with that emitted by their incandescent vapours. A thin coherent film of metal usually transmitted light of a colour remarkably similar to that emitted by its incandescent vapour, and if the films were perfect and continuous there would, in all probability, be no exceptions. The colour of the incandescent vapour of a metal is the resultant of the colours of the various rays emitted, and depends on the number and intensities of the rays, and the colour can therefore be fairly predicted on examining a table of wave-lengths and relative intensities of the spectral lines of the metal.

The author further observes that if the order of the electrical volatility of the metals, as given by Crookes, be compared with Lothar Meyer's curve of atomic volumes, it will be found that the volatile metals lie at, or near, the minima of the curves, close together on the ascending sides in the periods IV, V, and VII, alternating from one to the other. Magnesium and aluminium, which are practically non-volatile, lie on the descending side of period III. Aluminium, which is less difficult to volatilise than magnesium, is nearer the minimum of the curve. G. T. M.

Laws of Electrolysis. By A. Chassy (*Compt. rend.*, **114**, 998—1000).—In order to avoid exceptions, the author proposes to substitute the following statement for the statements of Faraday, Becquerel, and Wiedemann:—*When any substance whatever is electrolysed, there is always liberated an equivalent of hydrogen or the corresponding quantity of the electro-positive radicle.* He finds that in the electrolysis of potassium ferricyanide there are liberated K_3 and $FeCy_6$; with sodium nitroprusside, Na_2 and $FeCy_5NO_2$; whilst with basic ferric nitrate $Fe_2O_3,2N_2O_5$, the products are Fe_2 and $2N_2O_5 + O_3$.

C. H. B.

Thermoelectric Phenomena at the Contact of Two Electrolytes. By H. Bagard (*Compt. rend.*, **114**, 980—982).—A thermoelectric couple consisting of two electrolytes, such as dilute sulphuric acid and a solution of zinc sulphate, or dilute sulphuric acid and a solution of cupric sulphate, shows variations with the temperature similar to those observed with a couple formed by an amalgam and an electrolyte. With the zinc sulphate, the E.M.F. at first increases with the temperature, attains a maximum and then decreases; with cupric sulphate the E.M.F. increases, reaches a maximum at about 40°, then at 70° becomes *nil*, and afterwards again increases.

C. H. B.

Separation of Precipitates at the Boundary of Electrolytes. By G. Kümmell (*Ann. Phys. Chem.* [2], **46**, 105—112).—Faraday showed that if in the two limbs of a U-tube layers of pure water are placed above a saturated solution of magnesium sulphate in such a manner that the two liquids do not mix, and a current then passed, a separation of a precipitate of magnesium hydroxide occurs at the boundary of the magnesium sulphate solution, and the water which is below the negative electrode. Herrmann (*Götting. Nach.*, 1887, 342) found that zinc sulphate could be substituted for magnesium sulphate. The author has repeated these experiments, but in place of using solutions of the metallic sulphates in water, has found it convenient to make use of solutions prepared with gelatin, which solidify on cooling. The gelatin does not interfere with the occurrence of the phenomenon, while at the same time the admixture of the salt with the pure water, which otherwise is difficult to prevent, may be avoided. With solutions prepared in this manner it was possible to examine the behaviour of a number of different sulphates, but only with those of magnesium, zinc, cadmium, and aluminium was the occurrence of a precipitate observed. The separation of the hydroxide always takes place first at the negative electrode, the appearance of the precipitate at the boundary of the two liquids being of later occurrence. By suitable modifications in the method of carrying out the experiment it was ascertained that the phenomenon is due to the solid particles being carried mechanically from the negative electrode through the feebly conducting water by the electric current. H. C.

Electrical Conductivity of Substances in Mixed Solvents. By S. Arrhenius (*Zeit. physikal. Chem.*, **9**, 487—511).—When a portion of the water in the aqueous solution of an electrolyte is replaced by a non-electrolyte, such as alcohol, so that the total volume remains unchanged, the electrolytic conductivity of the solution diminishes. If the quantity of non-electrolyte added (x), does not reach more than 10 per cent. the conductivity of the solution may be expressed by the formula $l = l_0\left(1 - \frac{\alpha}{2}x\right)^2$, where l_0 is the conductivity of the pure aqueous solution, and α an empirical coefficient.

The author has investigated 55 different electrolytic solutions with regard to the influence on their conductivity of six non-electrolytes (methyl alcohol, ethyl alcohol, isopropyl alcohol, ether, acetone, and cane sugar), the strengths of the solutions and the quantities of non-electrolyte added being varied. The decrease of the conductivity brought about by the addition of 1 per cent. by volume of the non-electrolyte (α) depends on the nature both of the electrolyte and of the non-electrolyte, varying between 1·5 and 4 per cent. of the conductivity of the pure aqueous solution. As the concentration of the electrolyte increases, α is in general the greater; and the variability of α with the concentration is such that it is smaller, the greater the degree of dissociation of the electrolyte is.

The diminution of the conductivity by the addition of a non-electrolyte is partially due to the increase of the fluid friction of the

solution, which lowers the speed of the ions. In the case of substances that are strongly dissociated (most salts, and strong acids and bases), the diminution is due almost entirely to this cause, and the relation between it and the increase of fluid friction may be expressed by the formula $1000\alpha = C + 1000C'(A - 1)$, where A is the fluid friction (compared to that of water as unity) of a solution with 1 per cent. of the water replaced by the non-electrolyte, and C and C′ are constants, which are the same for various groups of electrolytes. Here the addition of the non-electrolyte does not alter the degree of dissociation. On the other hand, when the dissolved substances are only feebly dissociated, the addition of the non-electrolyte not only diminishes the speed of the ions but also diminishes their number. This diminution of the degree of dissociation is greatest with non-electrolytes that contain no hydroxyl groups, becoming less as the number of hydroxyl groups in the molecule increases.

Temperature has only a slight influence on the proportional diminution of the conductivity, this diminution, however, becoming always smaller as the temperature rises.

The author indicates how to correct the observed conductivity of a solution for fluid friction, so as to reduce the value obtained to that in a liquid whose fluid friction is equal to that of pure water; and, finally, points out the method of applying his results to the determination of the ash in sugar solutions (molasses) by means of observations on the electrolytic conductivity. J. W.

Mechanical Determination of the Boiling Points of Compounds with Complex Terminal Substitution. By G. Hinrichs (*Compt. rend.*, **114**, 1272—1274).—The connection between the boiling points of compounds and the moment of inertia of the molecule round its natural axis of rotation has already been shown by the author in former papers. The application of the general formulæ obtained to the special case of the change of the normal paraffins into alcohols, and of the alcohols into the corresponding acids, is here considered. In a chain of n carbon atoms, the substitution of the mass μ for hydrogen will bring about an alteration of the boiling point $\Delta t = \frac{k}{n}\Sigma\mu\nu^2$, or the rise in the boiling point of a normal paraffin produced by complex terminal substitution is proportional to the sum of the reduced moments introduced, and inversely proportional to the number of carbon atoms in the paraffin. k is not, however, absolutely constant, but its value generally is proportional to the ordinate y_2 of the parabolic curve for the boiling points of the paraffins (*Compt. rend.*, **112**, 1128). H. C.

Mechanical Determination of the Boiling Points of Alcohols and Acids. By G. Hinrichs (*Compt. rend.*, **114**, 1367—1370).—Application of the formula obtained in a former paper (see preceding abstract) for the determination of the boiling points of alcohols and acids from those of the paraffins from which they are derived. The calculated values are found to agree well with those observed, and

the author predicts a boiling point of 212·4° for the normal nonyl alcohol. H. C.

Hydrogenation of Closed Rings: Constitution of Camphoric Acid. By F. Stohmann and C. Kleber (*J. pr. Chem.* [2], **45**, 475—499; compare Abstr., 1891, 376, 1146).—*Methyl dicarboxyglutarate*, $CH_2[CH(COOMe)_2]_2$, is prepared in like manner to the ethyl derivative (Abstr., 1888, 1061); it crystallises in large, brilliant prisms, melts at 48—48·5°, and dissolves easily in the usual organic solvents.

Methyl trimethylenetetracarboxylate (1, 1, 2, 2), $CH_2<\begin{matrix}C(COOMe)_2\\C(COOMe)_2\end{matrix}$, is obtained from methyl dicarboxyglutarate by dissolving it (1 mol.) in a little absolute methyl alcohol, adding sodium methoxide (2 mols.), cooling, and shaking with bromine (1 mol.). The methyl alcohol is then evaporated off and the liquid poured into water, whereby the new salt is separated. It crystallises in large prisms, and melts at 71·5—72°. When heated with fuming hydrochloric acid as long as methyl chloride is evolved, it yields the free acid which melts with evolution of carbonic anhydride at 215° (Abstr., 1890, 879).

Trimethylenedicarboxylic acid (1, 2) melts at 139° (compare Abstr., 1884, 992); the 1, 1 acid melts at 138·5—139° (Abstr., 1884, 832; Trans., 1885, 810). Tetramethylenetetracarboxylic acid (1, 1, 2, 2) melts at 138° (Trans., 1887, 22). Tetramethylenedicarboxylic acid (1, 1) melts at 158° (Trans., 1887, 5). Pentamethylenedicarboxylic acid (1, 2) melts at 161° (Trans., 1887, 244).

The table (p. 1041) shows the results of the author's calorimetric determinations on the above and other ring compounds; a few of the numbers have appeared before (Abstr., 1889, 1097; 1890, 100; 1891, 376), but are here repeated for the sake of coherence.

Each division in the table (excluding camphoric acid) represents successively the di-, tri-, tetra-, penta-, and hexa-methylene rings. It will be noted that the heat of combustion of the first member of each division does not increase over the one preceding it by 156·6 Cal. for the addition of CH_2, as is the case with homologues in the acetic series, even if maleïc acid be taken as the first member instead of fumaric acid. Further, the difference between the observed heat of combustion and that calculated on the basis of 156·6 Cal. increase in the case of the second and third members of the series is positive (+6·9 and +9·2 respectively when fumaric acid is the first member), whilst in the case of the fourth and fifth it is negative (−13·9 and −17·5 respectively), showing that more energy is consumed in closing the tetra-, tri-, and di-methylene rings than in closing the penta- and hexa-methylene rings.

When the numbers are compared for each addition of H_2, it will be noted that this addition, or, in other words, the opening of the ring to this extent, causes the following mean increase in the heat of combustion in Cals.:—In the dimethylene ring, 35·9; in the trimethylene ring, 31·9; in the tetramethylene ring, 29·1; in the pentamethylene ring, 52·9; in the hexamethylene ring, 54·7. The numbers that go to make up the mean for the dimethylene ring are not very concordant

Substance.	Formula.	Molecular weight.	Heat of combustion at constant pressure.	Heat of formation.
			Cal.	Cal.
Fumaric acid	$C_4H_4O_4$	116	320·1	193·9
Dimethyl fumarate	$C_6H_8O_4$	144	664·7	175·3
Maleïc acid	$C_4H_4O_4$	116	326·3	187·7
Succinic acid	$C_4H_6O_4$	118	356·8	226·2
Dimethyl succinate	$C_6H_{10}O_4$	146	703·6	205·4
1, 1-Trimethylenedicarboxylic acid	$C_5H_6O_4$	130	483·2	193·8
1, 2-Trimethylenedicarboxylic acid	$C_5H_6O_4$	130	484·1	192·9
1, 1, 2, 2-Trimethylenetetracarboxylic acid	$C_7H_6O_8$	218	483·0	382·0
1, 1, 2, 2-Tetramethyl trimethylenetetracarboxylate	$C_{11}H_{14}O_8$	274	1170·4	346·6
Glutaric acid	$C_5H_8O_4$	132	515·0	231·0
Methyl dicarboxyglutarate	$C_{11}H_{16}O_8$	276	1202·2	383·8
1, 1-Tetramethylenedicarboxylic acid	$C_6H_8O_4$	144	642·4	197·6
1, 2-Tetramethylenedicarboxylic acid	$C_6H_8O_4$	144	642·5	197·5
Adipic acid	$C_6H_{10}O_4$	146	668·9	240·1
1, 2-Pentamethylenedicarboxylic acid	$C_7H_{10}O_4$	158	776·0	227·0
Pimelic acid	$C_7H_{12}O_4$	160	828·9	243·1
Cis-hexahydroterephthalic acid	$C_8H_{12}O_4$	172	928·6	237·4
Fumaroïd-hexahydroterephthalic acid	$C_8H_{12}O_4$	172	929·5	236·5
Suberic acid	$C_8H_{14}O_4$	174	983·7	251·3
Camphoric acid	$C_{10}H_{16}O_4$	200	1244·3	247·1

among themselves, nor do they agree well with the numbers which the authors have previously obtained for ethylenic linking (Abstr., 1891, 376). On the other hand, those for the hexamethylene ring are fairly constant between 54 and 55. The mean energy lost by the addition of H_2 is, in Cals:—33·1 for the dimethylene ring; 37·1 for the trimethylene ring; 39·9 for the tetramethylene ring; 16·1 for the pentamethylene ring; and 14·3 for the hexamethylene ring.

The structures which have been ascribed to camphoric acid are:—(1) An open chain with one ethylenic linking (Kekulé); (2) a derivative of tetramethylenedicarboxylic acid (Ballo-Brühl); (3) a ketoxycarboxylic acid (Friedel); (4) a hexamethylene derivative of various structure (*a*, Wereden; *b*, Oddo; *c*, Kachler; *d*, Armstrong; *e*, the authors). The authors have calculated the heat of combustion of camphoric acid on the basis of each of the formulæ which have been given (for which see the authors quoted), and find that their

experimental number agrees most closely with the number calculated for Armstrong's formula. The figures are as follows, the bracketed numbers referring to those given above:—Calculated (1) 1255·7; (2) 1268·9; (3) 1257·1; (4) *a*, 1242·2; *b*, 1241·9; *c*, 1244·7; *d*, 1244·1; *e*, 1242·0. Found, 1244·3. A. G. B.

Thermal Function of Phenol. By de Forcrand (*Compt. rend.*, **114**, 1010—1012).—Pure sodium and potassium phenoxides were obtained by mixing a solution of sodium or potassium ethoxide in excess of alcohol with an alcoholic solution of phenol, evaporating to dryness in a current of hydrogen, and heating at 135° in order to expel the last traces of alcohol. The sodium compound forms a hard, white crystalline, deliquescent mass, and the potassium compound is similar, but is always slightly coloured.

The thermal results were as follows:—

Heat of dissolution C_6H_5NaO between 13° and 16′	=	+9·35 Cal.
„ „ C_6H_5KO „ „		+7·13 „
C_6H_6O diss. + NaOH diss.	develops	+7·96 „
C_6H_6O „ + KOH „	„	+8·20 „
C_6H_6O sol. + Na sol. = C_6H_5NaO sol. + H gas	develops	+39·10 Cal.
C_6H_6O sol. + NaOH sol. = C_6H_5NaO sol. + H_2O sol.	„	+ 7·23 „
C_6H_6O sol. + K sol. = C_6H_5KO sol. + H gas	„	+46·28 „
C_6H_6O sol. + KOH sol. = C_6H_5KO sol. + H_2O sol.....	„	+12·41 „

The thermal value of the ordinary phenolic function (+39·10 Cal.) is therefore little greater than that of glycol or erythritol, and is lower than that of glycerol. Even taking into account the exaggerations of the value of the first alcoholic function arising from the causes explained in former papers, phenol approaches more nearly to the alcohols, and more especially to the tertiary alcohols, than to the acids. The value for phenol, +39·10 Cal. is, in fact, almost identical with the mean (+39·03 Cal.) of the values of trimethylcarbinol and acetic acid. C. H. B.

The Heat of Dissolution of Gases in Liquids. By S. U. Pickering (*Phil. Mag.* [5], **34**, 35).—Various substances, of which the heat of vaporisation was known, were dissolved as liquids in water, acetic acid, and benzene separately, and thence their heat of dissolution in the gaseous condition was calculated. The values obtained were in all cases considerable, 5500 to 14000 cal. per gram molecule, showing that there is a considerable loss of potential energy, even when gases dissolve in liquids (to form solutions which are non-electrolytes), and that the dissolved substances cannot be present in a condition analogous to that of a free gas. The heat evolved depends on the nature both of the solvent and of the dissolved substance, and

no numerical relations between the values in the various cases was observed. With water as a solvent the heat evolved is generally greater than with acetic acid or benzene, thus agreeing with the known tendency of water to form molecular compounds. The author then answers *seriatim* the criticisms which J. Walker passed (this vol., p. 264), on his freezing-point determinations and on his arguments against the dissociation theory. S. U. P.

Density of Liquefied Gases and their Saturated Vapours and Critical Constants of Carbonic Anhydride. By E. H. Amagat (*Compt. rend.*, **114**, 1322—1326).—Discussion of the curves given in a former paper (this vol., p. 934) for the densities of liquid carbonic anhydride and its saturated vapour. H. C.

Volume Lag and its Bearing on Molecular Constitution. By C. Barus (*Amer. Chem. J.*, **14**, 191—202).—In studying the relation between melting point and pressure, it was found that the pressure necessary to solidify a substance was decidedly greater than the pressure at which it again passes into the liquid state. At first it seemed that the differences so obtained might be referred to heating effects on compression and to cooling on expansion, but the magnitude of the interval obtained is often too large for this interpretation. If the maximum pressure at which the substance just remains liquid, persistently exceeds the minimum pressure under which it just remains solid, then the observed phenomenon is a true volume lag (hysteresis).

The author assumes, in explanation of the above fact, the existence of cohesive affinities among the atoms, which are of the same nature as those which are active in effecting chemical combination. Change of state of aggregation is brought about by, and is evidence of, a corresponding change of the cohesive valency in one or more of the constituent atoms of the substance. It is shown that this view is in keeping with many physical and chemical properties of substances in addition to that which is noted above. H. C.

Absorption Coefficients of Gases. By F. Henrich (*Zeit. physikal. Chem.*, **9**, 435—443).—The author has recalculated the temperature equations for the absorption coefficients of gases by means of the method of least squares from Bunsen's experiments. His results are as follows :—

Nitrogen in alcohol—

$$C = 0{\cdot}12637 - 0{\cdot}00042813t + 0{\cdot}0000063046t^2$$

Hydrogen in alcohol—

$$C = 0{\cdot}0693 - 0{\cdot}00016654t + 0{\cdot}0000017445t^2$$

Butane in water—

$$C = 0{\cdot}030827 - 0{\cdot}00092585t + 0{\cdot}00002384t^2$$

Carbon monoxide in water—

$$C = 0{\cdot}032784 - 0{\cdot}00080094t + 0{\cdot}000015872t^2$$

Methane in water—

$$C = 0{\cdot}05473 - 0{\cdot}0012265t + 0{\cdot}000011959t^2$$

Methane in alcohol—

$$C = 0{\cdot}522745 - 0{\cdot}00295882t + 0{\cdot}0000177001t^2$$

Ethane in water—

"Methylgas"

$$C = 0{\cdot}085576 - 0{\cdot}0030389t + 0{\cdot}00004979t^2$$

"Aethylwasserstoff"

$$C = 0{\cdot}0939012 - 0{\cdot}0034106t + 0{\cdot}0000547035t^2$$

Ethylene in water—

$$C = 0{\cdot}25487 - 0{\cdot}0088312t + 0{\cdot}00017417t^2$$

Ethylene in alcohol—

$$C = 3{\cdot}5846 - 0{\cdot}056153t + 0{\cdot}00062369t^2$$

Carbonic anhydride in water—

$$C = 1{\cdot}7326 - 0{\cdot}066724t + 0{\cdot}0012394t^2$$

Carbonic anhydride in alcohol—

$$C = 4{\cdot}3294 - 0{\cdot}094261t + 0{\cdot}0012354t^2$$

Nitrous oxide in water—

$$C = 1{\cdot}30263 - 0{\cdot}046254t + 0{\cdot}00072154t^2$$

Nitrous oxide in alcohol—

$$C = 4{\cdot}1902 - 0{\cdot}074389t + 0{\cdot}00078226t^2$$

Nitric oxide in alcohol—

$$C = 0{\cdot}31578 - 0{\cdot}003469t + 0{\cdot}00004827t^2$$

Hydrogen sulphide in water—

$$C = 4{\cdot}4015 - 0{\cdot}089117t + 0{\cdot}00061954t^2.$$

The probable errors of these equations are much less than those of the equations given by Bunsen. J. W.

Viscosity of Aqueous Salt Solutions. By C. Lauenstein (*Zeit. physikal. Chem.*, **9**, 417—434).—The author has determined the viscosity of aqueous solutions of a large number of the sodium salts of organic acids. The temperature chosen was 25°, and the solutions investigated were $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{1}{1}$ normal. The method of measurement was that described by Ostwald (*Lehrbuch*, 2nd ed., **1**, 550). The coefficient η varies in very many cases with the dilution according to the formula of Arrhenius, $\eta = A^n$ (where A is a constant depending on the nature of the dissolved substance, and n is the number of gram equivalents per litre); but in other cases, for example, the salts of the aromatic acids, the formula gives results which agree badly with experiment.

Certain regularities would seem to exist between the value of η for a given dilution of a sodium salt and the composition and constitution of the salt radicle. These regularities, however, are not of

so strict a nature as those observed in the case of the electric conductivity of the acids themselves, and are subject to many exceptions. J. W.

Theory of Solutions. By J. H. Van't Hoff (*Zeit. physikal. Chem.*, **9**, 477—486).—The author replies in this paper to some objections raised by Lothar Meyer against the osmotic pressure theory of solution. He shows that the osmotic pressure of a given solution is independent of the membrane, provided that this is really semi-permeable; and that the divergence of many of Adie's numbers (Trans., 1891, 344) from those required by the theory, is due to the partial permeability to the dissolved substances of the copper ferrocyanide membrane employed. He expresses complete indifference as to the mechanism of osmotic pressure. J. W.

The Cryoscopic Behaviour of Weak Solutions. Part II. Sodium Chloride and Copper Sulphate. Part III. Calcium Chloride and Nitrate. Part IV. Alcohol, Cane Sugar, Ether, and Urea. By S. U. Pickering (*Ber.*, **25**, 1314—1324, 1590—1599, 1854–1865).—Part II. Series of results with calcium chloride and copper sulphate were examined in the same way as in the case of the results with sulphuric acid (this vol., p. 678). Values calculated according to the conductivity when compared with the experimental values up to a depression of 1·66°, show a mean difference 374 times greater than the ascertained experimental error in the case of sodium chloride, whilst in the case of copper sulphate the discrepancy is far greater. On the other hand, a four-curve drawing which the author considers represents the results with sodium chloride, attributes an apparent error to the points agreeing exactly with the experimental error, and a similar result is obtained in the case of copper sulphate. The bridging over of any of the "breaks" in these figures increases the apparent error beyond legitimate limits.

Part III. *Calcium chloride and nitrate.*—Owing to the absence of data, the values for the calculated freezing points could not be obtained in these cases, but they could scarcely agree with the observed values in the case of calcium chloride, since the molecular depression with this salt was found to diminish generally with dilution, whereas supposed dissociation, and, consequently, the calculated molecular depression, must increase with dilution. In both cases it is shown that the author's interpretation of the results as curvilinear figures with breaks in them, agrees exactly with the magnitude of the experimental error, though this magnitude is very different in the two cases. The method is described by which the constant error, due to some of the solvents having separated before the freezing point, is observed when the "crystallisation" method is adopted; it consists in comparing the results given by this method with those given by determining the final melting point, as indicated by the rates at which the temperature of a partially crystallised solution rises before and after complete redissolution. The error was found to be 3·44 per cent. of the observed depression.

Part IV. *Alcohol, cane sugar, ether, and urea.*—The results with alcohol (up to a depression of 1·6°) indicated the existence of one

break, those with cane sugar two breaks, those with ether one break, and those with urea, none. The drawings made in accordance with these indications agreed exactly with the ascertained experimental error in each case, though this varied from 0·00050° to 0·00256° in different cases. The omission of any of these breaks, as in other cases, produces figures representing the existence of errors much greater than the known experimental errors, and the insertion of an imaginary break where none exists, does not improve the agreement with the experimental errors to any appreciable extent. A less complete examination of the results with cane sugar has been previously published (this vol., p. 109). The molecular depression with alcohol increases at first and then diminishes as the strength increases, with sugar it increases throughout, with ether it increases and then diminishes, whilst with urea it diminishes throughout. S. U. P.

Partially Miscible Solutions. By H. Pfeiffer (*Zeit. physikal. Chem.*, **9**, 444—476).—When 20 c.c. of amyl alcohol, 20 c.c. of ethyl alcohol, and 32·9 c.c. of water are shaken up together at the ordinary temperature, the mixture separates after a time into two layers. At 39·80° it remains perfectly homogeneous. If, instead of 32·9 c.c. of pure water, an equal volume of a dilute salt solution is added, the temperature at which the mixture no longer separates into layers is changed. Thus, for decinormal solutions, the following results were obtained, T representing the temperature of homogeneity for the solutions, and t that for pure water :—

	T.	t.	T − t.
Na_2CO_3.....	53·20°	39·80°	+13·40°
$BaCl_2$.....	50·00	,,	+10·20
KOH.....	47·85	,,	+ 8·05
NaCl.....	47·60	,,	+ 7·80
HCl.....	39·80	,,	0·00
AmCNS.....	34·10	,,	− 5·70

The author performed many experiments with isobutyl alcohol instead of amyl alcohol, using salt solutions of various strengths. He finds that the difference T − t = Δ increases with the valency of the salt, and that it is approximately proportional to the concentration of the salt solution. Analogous salts have equal differences, and the differences of true double salts are equal to the sum of the differences for their components. The increase of volume of the upper layer, just before complete mixture takes place, or the decrease of volume of the lower layer, is approximately proportional to the salt present. The same is true of the increase in the specific gravity of the layers. The difference Δ is dependent on the amount of salt that enters each layer, and the relation may be expressed by the formula $\Delta = K_2C_2 - K_1C_1$, where C_1 and C_2 are the molecular quantities of salt in 1 litre of each layer, and K_1 and K_2 are constants which are the same for analogous salts. Knowing the constants K_1 and K_2, the difference Δ, and the actual concentration of the two layers, it is possible to calculate the molecular weight of the dissolved substance. The agreement between theory and experiment is fairly good.

The author also made observations on the miscibility of various substances with water at different temperatures. Thus, the quantities of water given in the following table were added to mixtures of amyl and ethyl alcohol (whose composition is indicated by the first and second columns) before any milkiness appeared in the liquid:—

Amyl alcohol.	Ethyl alcohol.	Water at 9·10°.	Water at 19·20°.
3 c.c.	3 c.c.	3·21 c.c.	3·50 c.c.
3 „	6 „	10·35 „	10·80 „
3 „	9 „	18·34 „	19·10 „
3 „	12 „	27·47 „	29·15 „
3 „	15 „	41·25 „	43·15 „

Experiments with ethyl alcohol, water, and various ethereal salts, showed that isomeric ethereal salts have about the same miscibility with water, and that this decreases rapidly with the number of carbon atoms in the molecule. J. W.

Abnormal Dissolution: Saturated Solutions. By F. Parmentier (*Compt. rend.*, **114**, 1000—1003).—The compound of ether and bromine, $3Br_2,2Et_2O$, described by Schützenberger, dissolves readily in ether, but if increasing quantities of ether are added, there arrives a point at which the excess of ether separates from the solution, as already observed in the case of phosphomolybdic and silicomolybdic acids. The quantity of ether required to saturate the solution increases with the temperature, whereas in the case of the two acids referred to, the quantity of ether required decreases with the temperature. The following table shows the weight of ether bromide dissolved by 100 parts of ether at various temperatures:—

−13°.	6°.	12°.	22·5°.	32°.
632	561	462	302	253

The following definition of a saturated solution is framed with a view to meet all cases:—*When substances can, without combination, form a homogeneous liquid, the solution is said to be saturated when one of the bodies, added in excess to the solution, separates from that solution.* C. H. B.

Solubility of Double Compounds. By R. Behrend (*Zeit. physikal. Chem.*, **9**, 405—416).—The isomeric substances, benzylisoparanitrobenzaldoxime (α) and paranitrobenzylisobenzaldoxime (β) unite molecule to molecule to form a double compound ($\alpha\beta$). This double compound is almost entirely dissociated into its components in alcoholic solution, as is shown by observations on the boiling point. The author has made solubility experiments on various mixtures of α and β, in order to determine the influence of the mass of each on the solubility of the double compound in alcohol. Series of determinations were made at temperatures ranging from 9·4° to 14°. A week must elapse before a state of equilibrium is reached in the solutions. The following table exhibits the results obtained. Solutions I and II are solutions of the simple components α and β;

III contains α and β in equivalent proportions; IV is obtained from a mixture containing excess of α, and V from a mixture containing excess of β. The numbers in the columns express parts by weight in 100 parts of solution:—

Solution.	9·4°.		10·4°.		14°.	
	α.	β.	α.	β.	α.	β.
I	1·16	—	1·18	—	1·41	—
II	—	2·16	—	2·19	—	2·60
III	1·25	1·25	1·27	1·27	1·51	1·51
IV	1·23	1·24	1·38	1·26	1·62	1·47
V	0·75	2·23	0·75	2·29	0·93	2·70

These values agree very well with those deduced from the principle laid down by Nernst (Abstr., 1890, 3) for the reciprocal influence of the solubility of salts; it being possible on this basis to calculate the solubility of the mixtures from the solubility of the simple components and of the double compound. Calculation shows that the double compound only exists to the extent of 7—10 per cent. in the alcoholic solution, the remainder being dissociated. J. W.

Isomorphism. Part VI. By J. W. Retgers (*Zeit. physikal. Chem.*, **9**, 385—404).—Lehmann observed that ammonium chloride could form intimate mixtures with chlorides of the heavy metals, with which it is not isomorphous. The author has made experiments with many combinations of corresponding compounds in order to ascertain whether ammonium chloride is singular in this respect, or shares the property with other substances. When a drop of concentrated ammonium chloride solution is spread on a microscope slide, and a few grains of ferric chloride are added, it is observed that the chloride disappears rapidly, and that brown, birefringent crystals of the double salt, $4NH_4Cl,Fe_2Cl_6 + 2H_2O$, appear in its neighbourhood. Further off, cubes of ammonium chloride separate out, showing all shades, from deep reddish-yellow, through pale-yellow, to colourless. These crystals are quite homogeneous, and contain no enclosed particles of ferric chloride. They exhibit striking optical anomalies, being mostly composed of four sectors, which show marked double refraction, as is seen in the polarisation colours and the strong pleochroism from pale-yellow to brown. This behaviour is very different from what is observed in the case of isomorphous mixtures; and the crystalline forms, both of anhydrous ferric chloride and of the above-mentioned double salt, completely exclude the idea of a direct isomorphism.

Ammonium chloride also forms mixed crystals, of the same character as those in which ferric chloride is contained, with the following compounds:—Cobaltous chloride (hydrated), nickel chloride (anhydrous), manganous chloride, ferrous chloride, cadmium chloride,

zinc chloride, cupric chloride (very slight admixture), chromic chloride (in acid solution, violet). Magnesium chloride and aluminium chloride do not mix with ammonium chloride, as is indicated by the perfectly isotropic character of the crystals obtained.

Ammonium bromide does not form mixtures with any of the bromides corresponding with the chlorides mentioned above, nor does ammonium iodide with the corresponding metallic iodides. The nitrate and sulphate behave similarly. Methylammonium chloride does not mix with ferric chloride.

Potassium, rubidium, cæsium, sodium, thallium, and silver chlorides do not form mixed crystals with ferric chloride. On the other hand, lithium chloride can mix with ferric chloride, but not with cupric or cobalt chloride.

The author considers the double refraction observed in the mixed crystals to be due, for the most part, to internal tension, but also, to some extent, to the enclosed birefringent metallic chlorides.

In the second portion of this paper, the author discusses the position of tellurium in the periodic system, and maintains his suggestion (Abstr., 1891, 1152) that this element should be placed in the eighth group with an atomic weight greater than that of iodine. The evidence of its isomorphism with sulphur and selenium is in his opinion inconclusive. J. W.

Inorganic Chemistry.

Alcoholic Solutions of Ammonia. By Delépine (*J. Pharm.* [5], **25**, 496—497).—The following table gives the solubility of ammonia in ethyl alcohol of various strengths and at various tem-

Degree of alcohol.		100°.	96°.	90°.	80°.	70°.	60°.	50°.
Melting ice	weight of gas..	130·5	146·0	173·0	206·5	—	246·0	304·5
	density	0·782	0·783	0·800	0·808	—	0·830	0·835
	sol. coefficient.	209·5	245·0	302·5	390·0	—	504·5	697·7
10°	weight of gas .	108·5	120·0	137·5	167·0	—	198·25	227·0
	density	0·787	0·803	0·794	0·800	—	0·831	0·850
	sol. coefficient.	164·3	186·0	234·4	288·0	—	373·0	438·6
20°	weight of gas..	75·0	97·5	102·0	119·75	137·5	152·5	182·7
	density	0·791	0·788	0·795	0·821	0·829	0·842	0·869
	sol. coefficient.	106·6	147·8	158·3	190·5	223·0	260·8	338·2
30°	weight of gas	51·5	74·0	77·0	81·75	100·3	129·5	152·0
	density	0·798	0·791	0·796	0·826	—	0·846	0·883
	sol. coefficient.	97·0	106·7	114·0	121·6	—	211·6	252·0

peratures. The weight of gas contained in a litre of the solution saturated at 760 mm. is given, also the density of the solution, and the coefficient of solubility calculated from the foregoing data and the density of the solvent.

Methyl alcohol also dissolves enormous quantities of ammonia. A purified commercial alcohol containing less than 3 per cent. of acetone dissolves 40 per cent. of its weight, thus :—

0°	Weight of gas per litre	218·0
	Density	0·770
	Coefficient of sol.	425·0

J. T.

Compounds of Carbon and Silicon. By P. Schützenberger (*Compt. rend.*, **114**, 1089—1093).—A covered gas-carbon crucible, containing an intimate mixture of crystalline silicon (1 part) and silica (2 parts), is placed in a larger crucible, and well surrounded by lamp black; this second crucible is then placed in a third, and also packed with lamp black. After subjecting the whole to a bright red heat for several hours, and subsequently cooling, the friable contents of the first crucible are powdered and boiled with moderately concentrated hydrofluoric acid in order to dissolve the silica and a small quantity of silicon nitride, Si_3N_4, which is formed. No free silicon is present. The insoluble residue, containing nearly one-half of the silicon employed, is extracted with boiling concentrated hydrofluoric acid, and the green powder which remains analysed by fusion with potash, and by heating in a stream of chlorine. This substance is a new *silicon carbide*, SiC, formed, doubtless, by the action of carbon monoxide on the silicon. On treating it with chlorine at a low red heat, silicon chloride is evolved, leaving carbon and part of the carbide unchanged. After burning the carbon in a current of oxygen, a portion of the residue can be acted on by chlorine at a bright red heat, but the residue from this second treatment is not further attacked by chlorine. W. J. P.

Metaphosphates. By G. Tammann (*J. pr. Chem.* [2], **45**, 417—474; compare Abstr., 1891, 7).—The author has reinvestigated the metaphosphates, and in this paper details the preparation of the various salts enumerated in the following summary, with which he concludes. A notice of the methods adopted for determining molecular weight has already appeared (Abstr., 1891, 7).

1. The trimetaphosphates of Fleitmann and Henneberg (*Annalen*, 1848, **65**, 304) are now shown to be dimetaphosphates of the general formula $R_2'(PO_3)_2$.

2. Fleitmann's dimetaphosphates (*Ann. Phys. Chem.*, **78**, 233, 338) are trimetaphosphates of the general formula $R_3'(PO_3)_3$.

3. Of tetrametaphosphates, only Fleitmann's salt, $CuNa_2(PO_3)_4$, has been obtained.

4. The following pentametaphosphates are known :—$NH_4K_4(PO_3)_5 + 6H_2O$; $NH_4(NH_4)_4(PO_3)_5$; $NH_4Na_4(PO_3)_5$; $NH_4Li_4(PO_3)_5$.

5. The uncrystallisable hexametaphosphates, $Na_6(PO_3)_6$ and $Ag_6(PO_3)_6$, are obtained from Graham's soluble sodium metaphos-

phate (*Ann. Phys. Chem.*, **32**, 33), which is a mixture of the foregoing sodium salt with several other hexametaphosphates.

6. The soluble potassium, sodium, and lithium hexametaphosphates derived from the acid $H_2Na_4(PO_3)_6$ and the two insoluble salts $Ag_4K_2(PO_3)_6 + H_2O$ and $3Sr_2K_2(PO_3)_6 + 4H_2O$ are prepared from the ordinary insoluble potassium, lead, and lithium metaphosphates.

7. Octametaphosphates of the general formula $R_3''Na_2(PO_3)_8$ are obtained by fusing magnesium, cobalt, nickel, manganese, or zinc sulphate with sodium metaphosphate.

8. Ammonium decametaphosphate is formed when the ammonium dimetaphosphate of Fleitmann (*loc. cit.*) is heated between 200° and 250°, and from this, strontium, manganese, silver, and lead decametaphosphates, and the salt $K_9NH_4(PO_3)_{10} + 10H_2O$ can be prepared.

9. Gregory's tetrakaidecametaphosphate (*Annalen*, **54**, 94), $Mg_6Na_2(PO_3)_{14}$, completes the list of those metaphosphates whose constitutions can be said to be known.

The following salts are still of uncertain formula:—

1. The anhydrous and insoluble copper, manganese, cobalt, and zinc metaphosphates.

2. The anhydrous and insoluble lead, bismuth, barium, cadmium, and silver metaphosphates.

3. Maddrell's insoluble sodium metaphosphate (*Annalen*, **61**, 53).

4. Another insoluble sodium metaphosphate, obtained by keeping sodium metaphosphate in fusion.

5. The soluble crystalline potassium, sodium, and ammonium metaphosphates from glacial metaphosphoric acid.

6. The salts $(NH_4)_2Li(PO_3)_3 + 4H_2O$ and $K_2Li(PO_3)_3 + 2H_2O$, insoluble in cold water.

7. A series of soluble metaphosphates, of which the crystalline potassium salt has the composition $KPO_3 + 3H_2O$.

8. A series of soluble, crystalline metaphosphates, of which the salts $NaPO_3 + H_2O$ and $3KPO_3 + 2H_2O$ are known.

The author describes two metaphosphoric acids. The one, *α-metaphosphoric acid*, is obtained by heating orthophosphoric acid until it retains only as much water as is represented by the formula HPO_3; it is a soft, silky mass. The other, *β-metaphosphoric acid*, is obtained by heating orthophosphoric acid until it sets to a glassy mass on cooling; the potassium salt of this acid is insoluble in potassium hydroxide solution. The β-metaphosphates are more stable in water than the α-metaphosphates; they are all freely soluble in water, and the β-salts can be separated from the α-salts by crystallisation.

A. G. B.

Copper Sulphites. By S. B. Newbury (*Amer. Chem. J.*, **14**, 232—238).—When a slow current of sulphurous anhydride is passed for several hours through a 10 per cent. solution of copper sulphate containing a roll of thin sheet copper, the solution becomes almost colourless, and the metal is found to be covered with red crystals of cuproso-cupric sulphite, $CuSO_3,Cu_2SO_3 + 2H_2O$. This red salt may also be obtained on warming the dark-green solution of cupric sulphite, which is formed by passing sulphurous anhydride through well-cooled water containing pure precipitated cupric hydroxide in

suspension. All attempts to obtain a crystalline salt from the green solution of cupric sulphite were without success, as, in every case, a deposit of the red salt was soon formed. On exposure to the air, or, still better, on passing a current of air through it, the green solution eventually gave a precipitate of a bright, yellow-ochre colour, which, when air-dried, formed a bright-yellow powder. This substance was also formed on adding alcohol to the green solution, and is shown by its properties and analysis to be the *basic cupric sulphite*,

$$3CuO,2SO_2,1\tfrac{1}{2}H_2O.$$

It dissolves in dilute hydrochloric acid to a green solution, giving off sulphurous anhydride without separation of cuprous chloride, and in dilute sulphuric acid without separation of metallic copper. On boiling with water for a few minutes, the compound undergoes complete decomposition, a deep-blue solution of copper sulphate and a brown, insoluble substance being formed, which, by hydrochloric acid, is completely converted into cuprous chloride with liberation of sulphurous anhydride, and dissolves in sulphuric acid with liberation of metallic copper. This substance is in all probability *cuprous sulphite*, for, on continued boiling with water, sulphurous anhydride escapes and bright-red cuprous oxide is formed.

When moist basic cupric sulphite is exposed to the air, it is gradually oxidised, forming cupric sulphate, which may be dissolved out by water, leaving a yellowish-green, insoluble powder, which gives all the reactions of the original substance. It is probably a basic cupric sulphite of simpler constitution than the one described above. G. T. M.

Composition of Glass suitable for Chemical Utensils. By R. Weber and E. Sauer (*Ber.*, **25**, 1814—1819).—The authors give analyses and the numerical results of their experiments on the action of the liquids previously employed (compare this vol., p. 410) on green bottle glass, window glass, and very hard combustion tubing; in all three cases the glass was only slightly acted on by water and by acids, but to a much greater extent by the alkaline liquids.

F. S. K.

Manganese Compounds. By H. Schjerning (*J. pr. Chem.* [2], **45**, 515—530).—Christensen's manganic hydrogen pyrophosphate, $MnHP_2O_7$, is best obtained by adding manganic orthophosphate (Abstr., 1884, 399) to molten orthophosphoric acid in a platinum crucible at 220—230°, so long as it dissolves therein, and continuing the heating for 6—8 hours with frequent stirring until the mass has become semi-solid. While still warm, this product is thrown, in small portions, into cold water, the precipitate washed until free from phosphoric acid, and dried at 97°. It is "pansy-coloured" and of uncertain crystalline form; it undergoes oxidation when moist, and is readily decomposed by alkalis and acids, evolving chlorine with hydrochloric acid and yielding a precipitate of a higher oxide of manganese with sulphuric and nitric acids; when heated, it loses water and oxygen, and is converted into manganous metaphosphate. *Manganic potassium pyrophosphate*, $MnKP_2O_7$, is obtained by adding

the solution of manganic orthophosphate in molten orthophosphoric acid to molten potassium nitrate; after continuing the heating for a minute or two, the melt is poured on to iron or stone, and, when cold, treated with cold water. The new salt is somewhat darker than that just described, and more stable to acids and bases; it is insoluble in water. When heated, it becomes darker and then loses oxygen; when cooled by carbonic anhydride and ether it becomes much paler. The corresponding sodium salt has been prepared by Christensen (Abstr., 1884, 399). Manganic metaphosphate can be prepared by heating the solution of manganic orthophosphate in molten orthophosphoric acid at 350° until it has become pasty, and then treating it with cold water.

Potassium chromic hydrogen pyrophosphate, $Cr_2K_2H_4(P_2O_7)_3$, is prepared by dissolving 10 grams of chromic hydroxide in 65 grams of orthophosphoric acid at 150°, adding 30 grams of potassium carbonate, and heating at 250—260° for some time; the melt is washed with hot water and the insoluble salt dried at 130°. It is bright green and crystalline. At a red heat it gradually loses water. A green salt of doubtful composition was obtained by adding chromic hydroxide and orthophosphoric acid to fused potassium cyanate and subsequently washing the melt with water.

Manganous sodium metaphosphate, $MnNa(PO_3)_3$, is prepared by throwing successive small portions of a mixture of manganic orthophosphate (2 grams), orthophosphoric acid (3 grams), and microcosmic salt (10 grams) into a platinum crucible heated to dull redness, and heating until the mass is colourless. Treatment with water leaves the salt undissolved; it is colourless and crystalline.

The reaction between sodium hydrosulphide and potassium permanganate results in the production of manganese sulphide. That between a solution of sulphur (32 per cent.) in sodium hydroxide solution (30 per cent.) and potassium permanganate yields manganoso-manganic oxide at a high temperature and manganic peroxide at the ordinary temperature. A. G. B.

Iron in Bone-black. By B. Terne (*Chem. News*, **65**, 222—223). —The author finds that bone-black does not yield up its iron to solutions of citric acid, anyway not when a 0·1 or 0·25 per cent. solution of that acid is exposed for 24 hours at nearly 100° to bone-black containing as much as 0·5 per cent. of iron. In fact, he finds that fresh, regular sugar-house-black removed all the iron from citric acid solutions previously rendered dark yellow by the addition of one-tenth per cent. of that metal. A. Behr points out that there are three sources of iron in sugar-house-black:—1. The iron originally contained in the black. 2. The iron in the raw sugar. 3. The iron taken up by the liquors and the bone-black in the sugar refining. He adds that the removal of iron from the sugar only occurs when the black is fresh, and that as the black accumulates iron as it gets old, it even imparts some of that metal to the sugar passing through it; moreover, diluted sugar solution carries away a certain amount of iron, even from very good black. The initial iron in the black should obviously be reduced as low as possible, more especially as being in the

metallic state it can be easily removed by a magnetic separator. In fact, the author employs magnetic separation on a small scale for the rough estimation of iron in the black in the factory. D. A. L.

Mineralogical Chemistry.

Hungarian Minerals. By J. Loczka (*Zeit. Kryst. Min.*, **20**, 317—320).—In 1885 the author was requested by the Hungarian Academy of Sciences to examine 10 Hungarian minerals. The results of his investigation are as follows:—

1. *Antimonite from Felsöbánya.*—Sp. gr. 4·642. The composition is in accordance with the formula Sb_2S_3.

2. *Antimonite from Magurka.*—This mineral is dense, and of a grey colour. Sp. gr. 4·55.

Analysis gave—

Sb.	S.	Pb.	Cu.	Fe.	Quartz.	Total.
69·87	27·60	2·25	0·12	0·11	0·77	100·72

3. *Tetradymite from Zsupkó.*—Soft crystals of a sp. gr. of 7·581 gave, on analysis, results corresponding with the formula $2Bi_2Te_3,Bi_2S_3$.

4. *Hessite from Botes.*—The crystals contain silver, tellurium, gold, and traces of iron. Sp. gr. 8·39. Formula $(AgAu)_2Te$.

5. *Tellurium from Faczebaya.*—Formerly it was impossible to obtain pure material, as it was so intimately associated with quartz and pyrites. An analysis of mineral of this character yielded 80·39 per cent. of tellurium, whilst an analysis of rounded crystals of a sp. gr. 6·084 recently found, yielded 97·92 per cent. of tellurium with gold, iron, copper, quartz, and traces of selenium.

6. *Hæmatite from the Hargita Mountains.*—This mineral has a sp. gr. of 5·289, and gave, on analysis, the following results:—

Fe.	O.	Sn.	Insoluble.	Total.
69·92	28·99	0·52	0·15	99·58

7. *Tetradymite from Rézbánya.*—Sp. gr. 7·022. Analysis gave results corresponding with the formula $2Bi_2Te_3,Bi_2S_3$.

8. *Fauserite from Hodrusbánya.*—This salt has a reddish-violet tinge and a bitter, metallic taste. Sp. gr. 1·67. The author has made six partial analyses, and the mean results are in good accord with the formula $SO_4(Mg,Zn,Co,Fe),7H_2O$.

9. *Rock-salt from Torda.*—Sp. gr. 2·205. The mean of six analyses is appended (Analysis A).

10. *Rock-salt from Vizakna.*—This salt is grey, and mixed with a little earthy matter. Sp. gr. 2·186. The mean of seven analyses is as follows (B):—

	Na.	Cl.	Fe.	Ca.	SO_4.	Mg.	H_2O.	Insol.	Total.
A.	39·362	60·592	0·012	0·008	0·007	0·005	0·015	0·056	100·057
B.	39·356	60·572	0·005	0·013	0·017	0·007	0·024	0·065	100·059

B. H. B.

Martite. By A. Lavenir (*Zeit. Kryst. Min.*, **20**, 271; from *Bull. soc. fran. min.*, **12**, 49).—The examination of some very fine octahedra of martite from Brazil, showed that the substance, which was soluble only in *aqua regia*, yielded, on heating to redness in a current of hydrogen, a quantity of water exactly corresponding with the formula Fe_2O_3. The sp. gr. is 5·194—5·205; whilst it should be, if the substance had been formed from iron pyrites without change of volume, two-thirds of 5. The homogeneity of the material examined appears to be evidence against a pseudomorphous origin. B. H. B.

Brookite, Octahedrite, Quartz, and Ruby. By G. F. Kunz (*Amer. J. Sci.*, **43**, 329—330).—The author records an interesting discovery of minerals at Placerville, Eldorado Co., California, in a decomposed vein of crystallised quartz. Some of the quartz crystals weigh 90 lbs., and are pellucid and free from flaws. Octahedrite and brookite are found implanted on the quartz.

Very large ruby crystals have recently been found in the mines of Burma, some having weighed 300 to 2000 carats. They afford, however, but little fine ruby for cutting. One crystal examined by the author was a perfect, doubly terminated, hexagonal prism, 29 mm. in height. It weighed several ounces, and was valued at £200.

B. H. B.

Fluorine in Natural Phosphates. By A. Carnot (*Compt. rend.*, **114**, 1003—1006).—The author has determined the proportion of fluorine in many varieties of natural phosphates, using the method of estimation previously described (this vol., p. 911).

Direct estimation of the fluorine in apatites verifies the ordinary formula $3Ca_3(PO_4)_2 + Ca(F,Cl)_2$. Fibrous semicrystalline phosphorites have almost exactly the same composition as apatite. Earthy or compact and slightly concretionary phosphorites contain less fluorine. Distinctly concretionary phosphorites contain only from 0·05 to 1·38 per cent. of fluorine. The presence of the smaller proportion of fluorine in the less crystallised varieties is noteworthy in connection with the well-known mineralising effect of fluorine.

In almost all the 12 varieties of sedimentary phosphates examined the ratio of fluorine to phosphoric acid was the same as in apatite. This result agrees with that obtained by H. Lasne. C. H. B.

Cuprodescloizite from Mexico. By F. Pisani (*Zeit. Kryst. Min.*, **20**, 270—271; from *Bull. soc. fran. min.*, **12**, 38).—The author has analysed the mineral from Zacatecas, which occurs in cavities in a vein of galena, and has a greenish-black or brown colour, and a sp. gr. of 6·06. The analytical results were as follows:—

As_2O_5.	V_2O_5.	PbO.	CuO.	ZnO.	H_2O.	Total.
4·78	17·40	53·90	8·80	11·40	3·20	99·48

From a study of previous analyses of similar vanadates, the author concludes that the descloizites examined by Damour and by Rammelsberg are different. Eusynchite and brackebuschite belong to the former, and dechenite is probably identical with eusynchite, as it also contains zinc. B. H. B.

Milarite. By F. P. Treadwell (*Jahrb. f. Min.*, 1892, i, Mem. 167—168).—Hitherto but few analyses have been made of the mineral milarite discovered by Kenngott. A new analysis of 0·6662 gram of absolutely pure material gave the following results:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	MgO.	Total.
72·79	10·12	11·32	4·32	0·26	1·19	trace	100·00

These results correspond with the formula $R_2O,2CaO,Al_2O_3,12SiO_2$. This formula is also in accord with the results of Ludwig's analysis, but less so with those of Frenzel's and Finkener's analyses. B. H. B.

Gismondine from Westphalia. By F. Rinne (*Zeit. Kryst. Min.*, **20**, 302; from *Sitz. preuss. Akad.*, 1889, 1027).—In the cavities in the melilite-basalt of Hohenberg, in Westphalia, transparent crystals of gismondine occur, apparently in tetragonal pyramids. Optical examination shows, however, that they belong to the monosymmetrical system. The optical characters of the crystals are fully described, but no analysis of the mineral is given by the author. B. H. B.

Cordierite as Contact Mineral. By Y. Kakuchi (*Jahrb. f. Min.*, 1892, i, Ref. 233—235; from *J. Coll. Sci. Imperial Univ. Japan*, **3**, 313—334).—At the Watarasegawa, on the borders of the provinces of Shimotsuke and Kodsuke, Japan, there is a granite mass, 6 miles long and 1 mile wide, surrounded by palæozoic rocks, which are altered at the contact with the granite, and the slate which occurs in immediate vicinity of the granite contains cordierite crystals. On analysis, these crystals gave the following results:—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
48·43	32·36	8·55	1·32	0·46	7·81	1·55	100·48

from which results the author deduces the formula

$$6MgO,4FeO,10Al_2O_3,25SiO_2.$$

The hardness of the mineral is 7, and its sp. gr. 2·642. For this contact cordierite, which differs in several respects from the ordinary variety, the name of *cerasite* is suggested. B. H. B.

Fouquéite, a New Mineral. By A. Lacroix (*Zeit. Kryst, Min.*, **20**, 290; from *Bull soc. fran. min.*, **12**, 83).—From the anorthite-gneiss of Madras, the author has isolated monosymmetrical crystals of a lemon-yellow colour. Analysis yielded:—

SiO_2.	Al_2O_3.	FeO.	CaO.	Loss on ignition.	Total.
38·3	31·9	4·4	23·5	2·7	100·8

The sp. gr. is 3·31. The mineral may be a dimorphous modification of zoisite. B. H. B.

Peridotite in Central New York. By C. H. Smyth (*Amer. J. Sci.*, **43**, 322—327).—In view of the interest attaching to the demonstration by G. H. Williams of the igneous nature of the so-called serpentine of Syracuse, New York, the author regards a further occurrence of similar rocks at Mannheim, New York, as worthy of note. The highly basic character of the Mannheim rock is shown by the following partial analysis:—

Loss on ignition.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.
15·20	33·80	6·84	12·26	9·50	21·38

The microscopical and chemical evidence brought forward by the author shows that the rock of the Mannheim Dyke is a member of the peridotite group, and probably of the same age as the dykes of Syracuse and Ithaca in New York. B. H. B.

Minerals from the Chrome Iron Ore Deposits of Maryland. By A. C. Gill (*Zeit. Kryst. Min.*, **20**, 285; from *Johns Hopkins Univ. Circ.*, **75**).—In fissures in the chromite of Montgomery Co., there occur chrome-tourmalin (Analysis I) in dark-green needles and fuchsite (Analysis II) in a greenish-white, chlorite-like mineral.

	SiO_2.	B_2O_3.	F.	P_2O_5.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	NiO.
I.	36·56	8·90	0·06	0·04	0·09	32·58	4·32	0·79	0·05
II.	42·21	—	—	—	—	34·55	2·03	1·03	—

	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	0·75	9·47	2·22	0·13	3·74	99·69
II.	0·47	3·13	0·82	9·16	6·77	100·17

B. H. B.

Chromiferous Clay from Brazil. By A. Terreil (*Compt. rend.*, **114**, 983—984).—The clay obtained from the Tocantins, near Cametà, is malachite-green in colour, has a waxy appearance, and is very friable. It melts before the blowpipe and forms a flesh-coloured enamel, the green chromium oxide being converted into the red or ruby oxide. The clay has the composition:—

SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
46·20	18·18	1·69	0·92	1·23	3·94	26·64	98·80

C. H. B.

Azure-Blue Pyroxenic Rock from New Mexico. By G. P. Merrill and R. L. Packard (*Amer. J. Sci.*, **43**, 279—280).—On the Gila river, a finely saccharoidal rock of beautiful, light, azure-blue colour occurs in nodular masses in a granular, crystalline, serpentinous limestone, and under the microscope is seen to consist wholly of colourless pyroxene interspersed with calcite. A piece of the blue

rock, free from serpentine, was pulverised, treated with warm hydrochloric acid to remove calcite, and then boiled in an alkaline carbonate. The analysis gave the following results :—

SiO_2.	MgO.	FeO.	CaO.	Total.
54·30	18·33	1·11	25·00	98·74

This reduces to the formula $CaMgSi_2O_6$, which is that of malacolite. The blue colour appears to be due to ferrous oxide. B. H. B.

Melilite-bearing Rock from Canada. By F. D. Adams (*Amer. J. Sci.*, **43**, 269—279).—At Ste. Anne de Bellevue, near Montreal, in 1877, a dyke was discovered during the progress of some blasting operations in the bed of the Ottawa river. The rock was, for the most part, much decomposed, and its true character was not recognised until the discovery by Törnebohm, in 1882, of melilite-basalt on the Island of Alnö, in Sweden. The Swedish and Canadian rocks are so similar that they are classed together by Rosenbusch as *alnoite*. An analysis of the Canadian alnoite gave the following results :—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2 H_2O.	Total.
35·91	0·23	11·51	2·35	5·38	13·57	17·54	2·87	1·75	9·40	100·51

This rock differs from the original alnoite from Alnö in containing much more olivine, and in being free from plagioclase.

B. H. B.

Serpentine Rock from Borzanasca. By C. Montemartini (*Jahrb. f. Min.*, 1892, i, Ref. 288; from *Atti Accad. Sci. Torino*, **35**, 209—212).—At Borzanasca, in Liguria, there is a green rock with distinct polar magnetism, containing bastite and small crystals of diopside, diallage, and chromite. Numerous white veins of chrysotile traverse the mass. An analysis of the rock (I) and of the mechanically isolated bastite (II) gave the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Cr_2O_3.	Loss on ignition.	Total.
I.	39·84	3·08	5·82	1·25	36·63	1·14	trace	12·86	100·62
II.	40·21	3·49	—	10·08	30·62	1·90	trace	13·23	99·53

B. H. B.

Rock of the Jiwaara, in Finland. By W. Ramsay and H. Berghell (*Jahrb. f. Min.*, 1892, i, Ref. 307—308; from *Geol. Fören. Förh.*, **13**, 300—312).—The authors have made an exhaustive study of the rock of the Jiwaara mountain, in Northern Finland, and, in the main, confirm the results given by Wiik in 1884. The main constituents are nepheline and pyroxene, with apatite, titanite, and titaniferous garnet (jiwaarite), and with calcite and cancrinite as secondary products. Felspar is absent. The rock belongs to the series of nepheline rocks, and for it the name of ijolite is proposed. Analyses of the rock and of the nepheline are given. B. H. B.

Monchiquite, a Rock of the Elæolite-Syenite Class. By M. Hunter and H. Rosenbusch (*Jahrb. f. Min.*, 1892, i, Ref. 321—322;

from *Min. petr. Mitth.*, **11**, 445—466).—This rock occurs over a large area in the provinces of Rio de Janeiro and Minas Geraës, in Brazil, in the form of narrow veins in gneiss near the contact with elacolite syenite. It is a black, massive rock, with porphyritic crystals of amphibole, pyroxene, mica, and olivine. Under the microscope, colourless, glassy magma, magnetite, and some apatite and plagioclase are seen. The authors give analyses of the glassy magma, the brown hornblende, the reddish-violet augite, and of two varieties of the rock.

B. H. B.

The Prehistoric and Kiowa Co. Pallasites. By O. W. Huntington (*Jahrb. f. Min.*, 1892, i, Ref. 266—267; from *Proc. Amer. Acad.*, **26**, 1—12).—The resemblance between the pallas irons recently found in Kiowa Co., Kansas, and the prehistoric specimens found in Ohio has been noted as being very striking. On further study, however, the author finds that the resemblance is not so remarkable as at first appeared, whilst a comparison with the famous Siberian pallasite and the prehistoric specimens show that they are almost identical. The Kiowa iron shows a far more perfect crystallisation than any other pallasite hitherto described. It also contains large quantities of chromite distributed through it; but no chromite is to be found in the prehistoric nor in the pallas meteorite. B. H. B.

Meteoric Iron from Colfax Township, North Carolina. By G. F. Kunz (*Jahrb. f. Min.*, 1892, i, Ref. 267; from *Trans. New York Acad. Sci.*, **9**, 197—198).—The meteoric iron from Colfax Township, Rutherford Co., is the same as that described by L. G. Eakins from Ellenboro, Rutherford Co. The mean of the following two new analyses is in good accord with that published by Eakins:—

	Fe.	Ni.	Co.	Cu.	P.	S.	Si.	Total.
I.	87·69	11·26	0·62	0·05	0·19	0·10	0·03	99·94
II.	89·22	9·37	0·53	0·04	0·19	0·08	0·01	99·44

B. H. B.

Meteoric Stone from Ferguson, North Carolina. By G. F. Kunz (*Jahrb. f. Min.*, 1892, i, Ref. 267; from *Trans. New York Acad. Sci.*, **9**, 198).—For the meteoric stone formerly mentioned by the author (Abstr., 1891, 279), 6 P.M. is given as the time of falling, and Ferguson, Haywood Co., North Carolina, as the locality.

B. H. B.

Meteorite of Misshof in Kurland, Russia. By B. Doss (*Jahrb. f. Min.*, 1892, i, Mem. 71—113),—On April 10, 1890, at 4 P.M., a meteoric stone was observed to fall on the Misshof estate in Kurland. The fall was accompanied by a loud report. The meteorite is now in the Riga Museum. Its original weight was about 5,800 grams and its sp. gr. is 3·79. It is covered by a dull, black crust $\frac{1}{4}$ to $\frac{1}{2}$ mm. in thickness, and the interior has a somewhat porous texture. It belongs to the chondrite class of meteoric stones. Under the microscope it is seen that fragments of olivine and rhombic pyroxene are associated with particles of iron and of magnetic pyrites, and with the characteristic chondræ forming a porous mass. The metallic portion, which

amounts to 23·77 per cent. of the mass, consists of 5·82 per cent. of magnetic pyrites and 17·95 per cent. of nickeliferous iron, the percentage composition of the latter being as follows:—

Fe.	Ni.	Cu.	Sn.
90·75	7·52	1·06	0·67

A preliminary determination of the composition of the meteorite gave:—

Nickeliferous iron	17·95
Magnetic pyrites	5·82
Silicates soluble in HCl	46·52
Silicates insoluble in HCl	29·26
Chrome iron ore	0·45
Substances soluble in water	0·12
Total	100·12

The memoir is accompanied by two plates and eight woodcuts.

B. H. B.

The Ljungby Meteorite. By O. Nordenskiöld (*Jahrb. f. Min.*, 1892, i, Mem. 138—140).—This meteorite fell in the parish of Ljungby, in Scania, on April 3, 1889, and was subsequently secured for the Stockholm Museum. It is a chondrite, not differing from the most usual type. Its sp. gr. is 3·61, and its composition is as follows:—

Fe.	Ni.	Co.	Cu.	FeO.	Al_2O_3.	NiO.	CaO.	MgO.	K_2O.
14·46	1·91	0·02	0·04	13·18	2·70	0·05	1·40	23·79	0·43

Na_2O.	SiO_2.	Cr_2O_3.	C.	S.	P.	Soluble in water.	Loss on ignition.
1·42	36·97	0·59	0·02	2·38	0·10	0·10	0·40

The composition of the portion soluble in mercuric chloride (nickeliferous iron) was—

Fe.	Ni.	Co.	Cu.	Total.
83·67	16·24	0·17	0·34	100·42

Analysis shows that the portion soluble in hydrochloric acid consists of fairly pure olivine, and that insoluble in acid consists of bronzite.

The various constituents are present in the meteorite in the following proportions:—

Nickeliferous iron	11·76
Olivine	40·98
Bronzite	38·86
Troilite	6·55
Iron phosphide	0·55
Chrome iron	0·87
Carbon and soluble salts	0·52
Total	100·09

Manganese and tin are not present. The high proportion of nickel in the nickeliferous iron is noteworthy. B. H. B.

Water and Basins of the Lakes of Aiguebelette, Paladru, Nantua, and Sylans. By L. Duparc and A. Delebecque (*Compt. rend.*, **114**, 984—987).

Per litre.	Aiguebelette. Aug. 26, 1891.	Paladra. Aug. 5, 1891.	Nantua. Feb. 25, 1892.	Sylans. Mar. 13, 1892.
Total residue..	0·1549	0·1682	0·1810	0·1750
SiO_2	0·0055	0·0042	0·0032	0·0015
CaO	0·0708	0·0845	0·0875	0·0710
MgO.....	0·0061	0·002	0·0071	0·0052
SO_3	traces	none	0·0042	0·0021
Cl	traces	traces	0·0001	traces

The calcium and magnesium are present chiefly as carbonates. The total solid matter in the affluents is, as a rule, not greatly different from the total solid matter in the lakes.

The basins of the lakes consist chiefly of silica, silicates, and calcium carbonate, with iron, aluminium, and magnesium. The proportion of silica and silicates is 7·15 to 27·15 per cent. in the case of Paladru, 6·90 to 33·80 at Nantua, 8·35 to 24·20 at Sylans, and 31·30 to 76·95 at Aiguebelette. C. H. B.

Organic Chemistry.

1 : 3-Dinitropropane. By F. Keppler and V. Meyer (*Ber.*, **25**, 1709—1714).—1 : 3-Dinitropropane may be obtained by the action of silver nitrite on trimethylene iodide. Dry powdered silver nitrite (3 mols.) is slowly added to the cooled iodide (1 mol.); a little ether is then added, and the mixture very gently warmed for some time. The silver salt is precipitated by ether, the solution filtered and evaporated; the residue is then again treated with silver nitrite (3 mols.). After precipitating the silver salt with ether, filtering and evaporating the ethereal solution, the residual oil is allowed to remain for some days at a low temperature, in order that all the silver iodide may separate. The oil is now dissolved in absolute alcohol, and on adding alcoholic sodium ethoxide, *sodiodinitropropane*, $C_3H_5(NO_2)_2Na$, separates as a white powder, and is repeatedly washed with alcohol and ether. It explodes violently on heating. Its aqueous solution gives a yellowish precipitate, which rapidly blackens with silver nitrate. Copper nitrate and lead acetate give yellowish precipitates, and mercuric chloride a white precipitate. Disodiodinitropropane could not be prepared. Dilute sulphuric acid liberates free *dinitropropane*, $CH_2(CH_2{\cdot}NO_2)_2$, from the aqueous solution of its sodium derivative; the solution is extracted with ether, the ethereal

solution dried by anhydrous sodium sulphate, and evaporated. The nitro-compound is then obtained as a yellow oil, which totally decomposes on distillation in a vacuum. After some days it becomes converted into a brown, viscid oil. The two other isomeric dinitropropanes can be distilled without decomposition, and have but few properties in common with 1 : 3-dinitropropane.

Trimethylene iodide is conveniently prepared by dissolving trimethylene bromide (1 vol.) in absolute alcohol (2—2·5 vols.), and digesting for two days with dry powdered potassium iodide (3 mols.) in a reflux apparatus on the water-bath. The solution is precipitated by ether, filtered, evaporated, and the residue again dissolved in alcohol and digested with potassium iodide (3 mols.), precipitated with ether, filtered, and the filtrate evaporated. The residual oil is freed from dissolved iodine by potash, and contains 92·3 per cent. of the iodide.

Trimethylene bromide reacts very violently with silver nitrite, giving a poor yield of dinitropropane.

Dinitropropanedisazobenzene, $CH_2[CH(NO_2)\cdot N_2Ph]_2$, is obtained by slowly adding an aqueous solution (10 c.c.) of diazobenzene sulphate (1·5 grams) to sodiodinitropropane (0·5 gram) and sodium acetate (0·5 gram) dissolved in water (10 grams). It separates as a gummy mass, which soon hardens, and is extracted by boiling alcohol; the residue separates from acetic acid in reddish-yellow needles, melts at 173°, and gives a cherry-red solution with concentrated sulphuric acid. It is soluble in hot acetic acid, chloroform, and ether, sparingly so in alcohol.

Dinitropropaneparadisazotoluene crystallises from acetic acid in beautiful yellow needles melting at 199°, and gives a yellow solution with concentrated sulphuric acid.

Dinitropropaneparadisazoanisoïl forms small, yellow needles melting at 181°, and gives a cherry-red solution with concentrated sulphuric acid.

Tetrabromo-1 : 3-*dinitropropane*, $CH_2(CBr_2\cdot NO_2)_2$, is obtained by slowly adding an aqueous solution (200 c.c.) of sodiodinitropropane (3·5 grams) to a saturated aqueous solution of bromine (8 grams); the liquid is subsequently made slightly alkaline with very dilute soda. More bromine is now shaken with the solution, and a flocculent precipitate separates; after again making alkaline, the precipitate is collected, washed with water, and crystallised from dilute alcohol. It forms silky needles, which melt at 98—99°, and, on strongly heating, decomposes with evolution of brown vapours.

Dinitropropane behaves in many respects like nitroethyl alcohol, and only partially as a nitro-compound. On reduction with zinc dust and acetic acid it yields ammonia. It gives the nitrolic acid reaction, and on heating with hydrochloric acid yields hydroxylamine, and, probably, malonic acid. W. J. P.

Nitropropylene. By P. Askenasy and V. Meyer (*Ber.*, **25**, 1701—1708).—*Sodionitropropylene* (*sodionitroallyl*), $C_3H_4Na\cdot NO_2$, is prepared by heating a mixture of perfectly dry silver nitrite and sand in a reflux apparatus at 40° with a solution of allyl iodide or bromide (1 vol.) in

ether (2—3 vols.) for 35—45 minutes. The colourless solution is filtered and allowed to remain for 12 hours, in order that the dissolved silver salt may separate. After the addition of absolute alcohol (2 vols.) to the filtered solution (1 vol.) the sodium compound is precipitated on addition of a solution of sodium ethoxide in absolute alcohol. The precipitate is collected, washed frequently with absolute alcohol and ether, and dried on a porous plate. The product obtained in this manner turns red on drying, owing to the retention of a little allyl iodide; if, however, the ethereal solution be distilled in a current of ether vapour before precipitation with sodium ethoxide, a little nitropropylene comes over, and on adding absolute alcohol and sodium ethoxide the sodium compound separates and retains its dazzling white colour on keeping. On treatment with concentrated sulphuric or hydrochloric acid, it carbonises with emission of light, and when slowly heated in a glass tube it explodes violently at 190—200°.

Nitropropylene is obtained by treating the aqueous solution of the sodium compound with the calculated quantity of dilute sulphuric acid and extracting with ether. The ethereal solution is washed with water and dried by anhydrous sodium sulphate; the ether is then distilled off, and the residual oil dried in a vacuum. The pure substance may also be obtained by distilling the ethereal solution in a current of ether vapour, and evaporating the distillate. It is a thick, brownish oil, which combines with bromine and polymerises to a black, tarry mass on remaining for some days. It explodes on heating, and cannot be distilled, without decomposition, under 20 mm. pressure.

Allylnitrolic acid, $CH_2{:}CH{\cdot}C(NO_2){:}NOH$, is prepared by slowly mixing ice-cold aqueous solutions (5 c.c. of each) of sodium nitrite (0·7 gram) and sodionitropropylene (1 gram); to the mixture is now slowly added concentrated sulphuric acid (1 gram) dissolved in water (5 c.c.). Dilute soda is added until the appearance of a permanent red colour, which is then destroyed by dilute sulphuric acid. The solution is now treated with excess of barium carbonate, filtered, acidified, and repeatedly extracted with ether. On evaporation of the ethereal solution, allylnitrolic acid separates in long needles, and may be crystallised from water. It melts at 68° in a capillary tube, but at 82—83° when in large quantities. It explodes violently with carbonisation at about 95°, and has a very pungent taste.

Nitropropyleneazobenzene, $NO_2{\cdot}C_3H_4{\cdot}N_2Ph$, is obtained by adding a concentrated aqueous solution of sodium acetate (0·5 gram) and diazobenzene sulphate (1 gram) to sodionitropropylene (0·5 gram), dissolved in a little water. It separates as an orange precipitate, which coagulates and turns deep red on standing. It crystallises from alcohol in red needles, and melts at 95—96° with decomposition. On heating with aqueous alcohol and cooling, it separates, mixed with a substance which crystallises in thin red scales.

Nitropropyleneparazotoluene, $NO_2{\cdot}C_3H_4{\cdot}N_2{\cdot}C_6H_4Me$, is prepared in a similar manner to the preceding compound, and crystallises from alcohol in brownish-red needles which melt at 95°.

Nitropropyleneorthazotoluene forms red needles melting at 85·5°.

With concentrated sulphuric acid it gives first, a brownish-yellow, and ultimately a dirty brown solution.

Nitropropyleneparazoanisoïl, $NO_2 \cdot C_3H_4 \cdot N_2 \cdot C_6H_4 \cdot OMe$, is very soluble in alcohol, and separates from the solution in brownish-red needles melting at 80°.

Nitropropyleneparazophenetoïl crystallises from alcohol in long, brownish-red needles, which melt at 94—95°. It gives a dark brown solution with concentrated sulphuric acid.

Nitropropylenemetazobenzoic acid, $NO_2 \cdot C_3H_4 \cdot N_2 \cdot C_6H_4 \cdot COOH$, is obtained in brick-red, nodular crusts, and is sparingly soluble in alcohol, ether, and chloroform. It decomposes at 145—150° without melting, and gives a reddish-yellow solution with concentrated sulphuric acid.

Nitropropyleneazometabromobenzene separates from absolute alcohol in light brown crystals, which melt at 93—94°. The corresponding *chloro*-derivative forms reddish-brown needles; it is very soluble in alcohol, and melts at 105·5°.

Nitropropyleneazopseudocumene crystallises in needles resembling alizarin. It is readily soluble in alcohol, melts at 104°, and gives an orange-brown solution with concentrated sulphuric acid.

On reduction with zinc dust and acetic acid, nitropropylene yields allylamine; with stronger reducing agents, ammonia is evolved. When heated with hydrochloric acid, nitropropylene gives acrylic acid and hydroxylamine.

Nitrobromopropylene, $CH_2{:}CH \cdot CHBr \cdot NO_2$, is prepared by the addition of bromine water to the aqueous solution of sodionitropropylene and subsequent extraction with ether. On evaporating the ethereal solution the bromide is obtained as a yellowish oil, which decomposes on heating.

Nitrotribromopropane, $CH_2Br \cdot CHBr \cdot CHBr \cdot NO_2$, obtained by the action of bromine on the monobromide, is a heavy, yellowish oil, which decomposes on heating, and evolves hydrogen bromide on keeping.

W. J. P.

Action of Organic Acids on Acetylenic Hydrocarbons. By A. Béhal and A. Desgrez (*Compt. rend.*, **114**, 1074—1077).—*Normal amylacetylene*, prepared by the successive action of phosphoric chloride and dry potash on œnanthaldehyde, boils at 101—102° under 750 mm. pressure; on heating it (1 part) with glacial acetic acid (4 parts) in a sealed tube at 280° for 24 hours, and subsequently fractionally distilling the product under reduced pressure, a mixture of the unchanged substance with a ketone is obtained. The fraction boiling above 120° is distilled with steam and treated with sodium hydrogen sulphite. On boiling the product with water, amyl methyl ketone is obtained as a liquid boiling at 149—150° under 755 mm. pressure.

Normal hexylacetylene is prepared by the successive action of phosphoric chloride and dry potash on hexyl methyl ketone, and boils at 126—126·5° under 753 mm. pressure; on heating with acetic acid as above described, it yields hexyl methyl ketone.

Butylmethylacetylene is obtained by the action of alcoholic potash on amylacetylene. It boils at 111—113° under 755 mm. pressure,

and does not combine with cuprous or silver salts. When heated with acetic acid it gives normal amyl methyl ketone.

Amylmethylacetylene, prepared by the action of dry potash on caprylene bromide, boils at 133—134° under 760 mm. pressure, and yields hexyl methyl ketone, boiling at 171°, when heated with acetic acid as above described.

On heating chloramylethylene, $C_5H_{11}\cdot CH{:}CHCl$, with silver acetate at 250°, amyl methyl ketone results; if the mixture be heated at 180°, however, it yields œnanthaldehyde.

The authors consider that these experiments show that an unstable acetate, $R\cdot CH{:}CH_2\cdot OAc$, is first formed on heating the hydrocarbon, $R\cdot C{:}CH$, with acetic acid, and that this undergoes hydrolysis with formation of an alcohol, $R\cdot C(OH){:}CH_2$, which then changes into the ketone, $R\cdot CO\cdot CH_3$. W. J. P.

Hydrocarbon derived from Perseïtol. By L. Maquenne (*Compt. rend.*, **114**, 1066—1069).—The author considers that heptine, C_7H_{12}, obtained by the action of hydriodic acid on perseïtol, is a cycloid hydrocarbon containing only one double bond. This view is supported by the fact of its ready conversion into toluene (Abstr., 1887, 565), its resemblance to the terpenes, and its colour reactions. The hydrocarbon of the composition C_7H_{14}, obtained by the reduction of heptine (*Compt. rend.*, **114**, 918), is a saturated hydrocarbon, and is not attacked by bromine, sulphuric acid, and cold nitric acid. Its molecular refraction, MR = 32·25 (Lorenz's formula) also shows it to be saturated. On treatment with chlorine, either in presence or absence of iodine, it yields hydrogen chloride and an oil which is carbonised by cold alcoholic potash and turned green by nascent hydrogen. Bromine and aluminium chloride convert the hydrocarbon into a resin with evolution of hydrogen bromide. It is most probably hexahydrotoluene, as its physical properties agree completely with those of that substance. W. J. P.

Action of Potassium Cyanide on Ammoniacal Cupric Chloride. By E. Fleurent (*Compt. rend.*, **114**, 1060—1061; compare this vol., p. 420).—On heating an ammoniacal solution (350 c.c.) of cupric chloride (21 grams), ammonium chloride (3 grams), and potassium cyanide (27 grams) in a sealed tube at 140—145° for four or five hours, an unstable double salt, $2Cu(CN)_2,NH_4CN,2NH_3 + 3H_2O$, is deposited in long, blue needles grouped in tufts. The crystals rapidly lose ammonia. On exposing the mother liquor to the air, ammonia is lost, and a very stable salt,

$$2Cu(CN)_2,Cu_2(CN)_2,2NH_3 + 3H_2O,$$

is deposited in large, rectangular, green scales. This compound is insoluble in water and decomposes at 100°. It is deposited unchanged from its ammoniacal solution, and, on treatment with dilute acids, yields cuprous cyanide with evolution of hydrogen cyanide. The mother liquor, after separation of this double salt, is colourless, and ultimately deposits two crystalline substances, which are now under examination.

The author estimates the cyanogen in these compounds by heating them in a sealed tube for two hours at 50—60° with concentrated nitric acid (1 vol.), silver nitrate, and water (2 vols.). This method is very rapid and gives good results. W. J. P.

Sodiotrimethylcarbinol: Value of the Tertiary Alcoholic Function. By De Forcrand (*Compt. rend.*, **114**, 1062—1064).—Trimethylcarbinol melts at 25·5° and has the sp. gr. 0·771 at 35·5°. The heat of solution of the crystalline compound in water (74 grams in 2 litres) is +3·50 Cal. at 5—8° and +3·23 Cal. at 13—15°. These values are comparatively high, and point to the existence of a hydrate like $C_4H_{10}O,H_2O$. On the addition of aqueous soda (1 equivalent in 2 litres) to the solution and allowing for the heat of dilution of the soda, −0·02 Cal. is liberated at 6—7°, and −0·06 Cal. at 14—16°; these numbers represent the calorific reaction between the alcohol and soda alone, and are of the same order as those obtained with the primary alcohols.

Sodiotrimethylcarbinol, C_4H_9ONa, is prepared as a white, pulverulent mass by heating finely-divided sodium with a large excess of the carbinol at 110° for 5—6 hours. The unchanged alcohol is eliminated by continued heating at 110° in a current of hydrogen. The heat of solution of the sodio-derivative in water (96 grams in 4 litres) is +18·30 Cal. at 15°.

From the above numbers the value of the function of solid trimethylcarbinol may be deduced as +27·89 Cal.; this is probably the value of the tertiary alcoholic function measured in the solid state. It differs by about 2 Cal. from the corresponding value for secondary alcohols (+29·75 Cal.) and by about 4 Cal. from that of primary alcohols (+32·00 Cal.). W. J. P.

Carbohydrates. By F. Ullik (*Chem. Centr.*, 1892, i, 432—433; from *Zeit. Brauwesen, München*, **15**, 15—17, 28—31, 39—41).—The carbohydrates, exclusive of the sugars, are grouped by the author as follows:—I, the amylums; II, cellulose; III, soluble starch; IV, dextrins; V, gums; VI, dextrin acids; VII, gum acids; VIII, pectins; IX, pectin acids.

The author considers that the last-named, the pectins and the "acid" bodies derived from them, belong strictly to the group of carbohydrates, because, on the one hand, glucoses may readily be obtained from them, whilst, on the other, substances corresponding with the pectins may be obtained from starch.

The addition of alkali, whether in excess or not, to the pectin acids, does not alter the rotatory power, and the same property belongs to some dextrins which have been obtained by the action of acids, and also to maltose. Pectin acids do not diffuse through a membrane, but their salts do so readily. The author separated a pectin acid from beetroot, the coefficient of rotation for which was $[\alpha]_D = 300$, and from which, by oxidation, 70—80 per cent. of mucic acid was obtained.

Soluble starch, cellulose, dextrose, and maltose all show the same rotatory power when dissolved in concentrated sulphuric acid.

Soluble starch appears to exist in different modifications, which are distinguished from one another in outward appearance, degree of solubility, and iodine reaction, but they all have the same rotatory power, namely, $[\alpha]_D = 199\,6—200\cdot8$. J. W. L.

First Product of the Reduction of Nitro-compounds with Stannous Chloride. By A. Kirpal (*Ber.*, **25**, 1714—1718).—The author shows that the methylhydroxylamine obtained by Hoffmann and Meyer (this vol., p. 291) by the reduction of nitromethane with stannous chloride is, as they supposed, identical with the β-methylhydroxylamine prepared by Dittrich (Abstr., 1891, 317) from β-benziledioxime methyl ether. The substance (1 mol.) obtained by both methods reduces Fehling's solution with production of equal quantities (2 mols.) of cuprous oxide. The hydrochloride melts at 85—90° and is very hygroscopic. On oxidation with Fehling's solution, methylamine and ammonia are obtained. No methyl alcohol is produced.

Nitroethane, nitropropane, nitropentane, and nitropropylene, on reduction with stannous chloride, yield bases which readily reduce Fehling's solution. Chloropicrin and bromonitroethane also give basic substances which contain halogen and are readily oxidised by Fehling's solution.

Negative results were obtained on attempting to reduce aromatic nitro-compounds with production of bases analogous to the foregoing. W. J. P.

Special Case of Isomerism. By R. Schiff (*Ber.*, **25**. 1690—1691).—When butylchloral hydrate reacts with an amide, two isomeric additive compounds are always formed. The mixture obtained on melting butylchloral hydrate with acetamide may be separated into an α-butylchloralacetamide, $C_6H_{10}Cl_3NO_2$, which is very sparingly soluble in boiling alcohol, and an isomeric β-butylchloralacetamide which is readily soluble in dilute alcohol. Corresponding isomeric additive products, whose melting points are given below, are obtained with other amides.

	Melting points.	
	α.	β.
Butylchloralacetamide	158°	170°
Butylchloralbenzamide.....	132	146
Butylchloralformamide	125	132

On distilling the α- and β-butylchloralacetamides with dilute sulphuric acid, two isomeric butylchloral hydrates, which both melt at 78°, are obtained. On treatment with nitric acid, they both yield trichlorobutyric acid, which gives ethyl salts boiling at 230—232°. The oximes derived from the α- and β-hydrates both melt at 65—66° and behave similarly towards acetic anhydride and alkalis. On melting the two hydrates with acetamide, however, they are found to yield the corresponding additive compounds having different melting points.

Two butylchlorals therefore exist, and can only be distinguished

by their behaviour towards amides, their melting points and other properties being identical. W. J. P.

Citronellic Aldehyde. By E. Kremers (*Amer. Chem. J.*, **14**, 203—212; compare Dodge, Abstr., 1890, 231; 1891, 285; and Semmler, Abstr., 1891, 539).—The substance employed by the author in his investigations was the so-called *citronellon*, from the oil of *Eucalyptus maculata*, var. *citriodora*, and was supplied by Schimmel of Leipzig. The oil was distilled under a reduced pressure of 15 mm., and the larger portion, which came over between 195° and 220°, was collected apart. It had a specific gravity of 0·875 at 21° and showed a rotatory power of $[\alpha]_D = +6·81°$. On analysis, numbers were obtained corresponding with the formula $C_{10}H_{18}O$, which is also in harmony with the general behaviour of the substance.

Citronellic aldehyde is an unsaturated compound and readily absorbs bromine in the ratio $C_{10}H_{18}O : Br_2$, but the additive product is so unstable that it can not be obtained in a crystalline condition. With sodium hydrogen sulphite, the crystalline solid, $C_{10}H_{18}O,NaHSO_3$, was formed, and from it the aldehyde was again liberated on treatment with sodium carbonate.

Citronellic aldehyde appears to form an oxime with hydroxylamine hydrochloride, but the compound was not isolated in a crystalline form. No satistactory condensation product was obtained with phenylhydrazine. On oxidation with ammoniacal silver oxide (compare Semmler, *loc. cit.*), the aldehyde gives an acid which forms a by no means characteristic silver salt, $C_{10}H_{17}O_2Ag$; whilst, with permanganate, it gives, in addition to oxalic and formic acids, two acids, the salts of which were not obtained in a sufficiently pure state to enable their composition to be determined. G. T. M.

Acetic Fluoride. By M. Meslans (*Compt. rend.*, **114**, 1020—1023).—Acetic fluoride can be obtained (1) by the action of acetic chloride vapour on silver fluoride heated at 300°; (2) by the action of acetic chloride on arsenic fluoride, the removal of the last traces of chlorine and arsenic being somewhat difficult; (3) by the action of acetic chloride on antimony fluoride in the cold, the product being kept in a closed glass vessel in contact with fragments of antimony fluoride; (4) by the action of acetic chloride on anhydrous zinc fluoride.

The last method is the best and most rapid. Zinc fluoride dried in a vacuum at 250° is added gradually to well-cooled acetic chloride. The vessel is then closed, and heated at 40° with agitation. The product is distilled, and collected in a well-cooled receiver, containing fragments of zinc fluoride. From this receiver it is distilled a second time, and is kept in perfectly dry glass vessels, hermetically sealed. Great care must be taken to avoid the presence of any moisture.

Above 19·5°, under atmospheric pressure, acetic fluoride is a colourless gas, does not fume in the air, and burns with a blue flame, producing water, carbonic anhydride, and hydrogen fluoride. Its odour recalls that of carbonyl chloride, and when inhaled its action is

not immediate, but in a short time it produces intense bronchial irritation.

Below 19·5° it is a very mobile, colourless liquid, miscible with alcohol, ether, and chloroform. It dissolves in all proportions in benzene, amyl alcohol, terebenthene, and glacial acetic acid. It does not mix with water or carbon bisulphide, but is slightly soluble in both of them. It dissolves very little iodine and no sulphur, but is dissolved in large quantity by bromine. At −23° its vapour tension is still 118 mm., and it does not solidify even at −55°; its vapour tension at the latter point is about 10 mm. Its vapour density is 2·163 (calc. 2·146). C. H. B.

Acetic Fluoride. By M. Meslans (*Compt. rend.*, **114**, 1069—1072; compare preceding abstract).—Acetic fluoride boils at 19·5°, and its vapour does not fume in the air. It is much more stable than acetic chloride. Water acts on it with production of hydrogen fluoride and acetic acid; the action is, however, much less vigorous than in the case of the chloride. Aqueous potash and soda have a similar action. Quicklime reacts with production of acetic anhydride. Ammonia acts on acetic fluoride with formation of pure, odourless acetamide. Aniline has a vigorous action on the fluoride, acetanilide and hydrogen fluoride being obtained. Acetic fluoride is soluble in all proportions in alcohol; no immediate action occurs, but after several hours ethyl acetate and hydrogen fluoride are formed. Amyl alcohol under similar conditions yields amyl acetate. Small quantities of acetic anhydride and sodium fluoride are obtained on heating acetic fluoride and sodium acetate in a sealed tube for four hours at 100°. Sodium and sodium amalgam have no appreciable action on the substance at ordinary temperatures, but at a low red heat, sodium decomposes it with incandescence, sodium fluoride, carbon, and a small quantity of liquid being formed. W. J. P.

Configuration of the Aldoximeacetic Acids or β-Oximidopropionic Acids. By A. Hantzsch (*Ber.*, **25**, 1904—1907).—The only representative of the aldoximeacetic or β-oximidopropionic acids has been prepared by Pechmann (Abstr., 1891, 1458), and all attempts to obtain an isomeride have been without success; the known compound must have the "anti-" configuration,

$$\begin{matrix} \mathrm{H{\cdot}C{\cdot}CH_2{\cdot}COOH} \\ \mathrm{HO{\cdot}N} \end{matrix} \quad ,$$

for unlike the only known modification of the oxime of acetoacetic acid (methylsynketoximeacetic acid), it does not under any circumstances yield an anhydride, and gives only a yellow coloration with ferric chloride, in place of the violet given by the acetoacetic derivative. Further, it very readily loses carbonic anhydride on boiling with water.

Although only one isomeride of the acid itself could be prepared, the acetyl compound appears to exist in two modifications; thus by the action of acetic chloride on the acid Pechmann obtained an acetyl compound melting at 145°, which is not acted on by a solution of

sodium carbonate, but is decomposed by soda, re-forming the original acid; this derivative gives a wine-red coloration with ferric chloride. If acetic chloride be replaced by acetic anhydride, an oily acetyl compound is formed, which is hydrolysed by sodium carbonate solution, and gives the same coloration with ferric chloride as the acid itself; if allowed to remain, it is slowly converted into the crystalline modification. Hence it appears that the acetyl derivative exists in two stereometric forms, the oily compound having the same configuration ("anti-") as the acid itself, and the second the syn-configuration.

$$\begin{array}{l} H\cdot C\cdot CH_2\cdot COOH \\ \quad\| \\ AcO\cdot N \end{array} \qquad \begin{array}{l} H\cdot C\cdot CH_2\cdot COOH \\ \quad\| \\ \quad N\cdot OAc \end{array}.$$

H. G. C.

Action of Ethyl Chlorocarbonate on Ethyl Sodacetoacetate. By L. Claisen (*Ber.*, **25**, 1760—1776).—The author and Zedel have previously shown (*Inaug. Diss., Munich*, 1889) that the interaction of sodacetylacetone and ethyl chlorocarbonate leads to the formation of two substances, namely, ethyl diacetoacetate,

$$CHAc_2\cdot COOEt,$$

and an isomeride which has probably the constitution

$$CHAc{:}CMe\cdot O\cdot COOEt;$$

the former has an acid character, forms a copper derivative, and gives an intense red coloration with ferric chloride in alcoholic solution, whereas the latter is a neutral substance, and gives neither of the reactions just mentioned.

The behaviour of ethyl sodacetoacetate with ethyl chlorocarbonate was found to be analogous to that of sodacetylacetone, the one product being ethyl acetomalonate, the other a compound, insoluble in alkalis, which has probably the constitution

$$COOEt\cdot CH{:}CMe\cdot O\cdot COOEt.$$

The latter reaction has also been recently studied by Michael (*J. pr. Chem.*, **37**, 473) and by Nef (this vol., p. 140). Michael isolated only the neutral compound to which he assigned the constitution given above, or the alternative formula

$$OEt\cdot C(CHAc)\cdot O\cdot COOEt,$$

which the author regards as highly improbable. Nef came to the conclusion that the neutral compound produced in the reaction is ethyl acetylcarbintricarboxylate, $CAc(COOEt)_3$, and assumed that the neutral compound described and analysed by the author was a mixture.

In the present paper the author proves conclusively that the neutral compound in question is not ethyl acetylcarbintricarboxylate but ethyl carboxethylacetoacetate.

Ethyl carboxyethylacetoacetate, $COOEt\cdot CH{:}CMe\cdot O\cdot COOEt$, is formed together with ethyl acetomalonate when solid, alcohol-free ethyl sodacetoacetate is gradually added to a well-cooled ethereal solution of excess of ethyl chlorocarbonate, and, after keeping for half an hour, the mixture warmed on the water-bath; it is a colour-

less oil, boiling at 130—131° under a pressure of 14 mm. Analyses of the carefully purified substance, vapour density determinations by Hofmann's method, and molecular weight determinations by Raoult's method in glacial acetic acid solution, all gave results agreeing well with those required by a compound of the molecular formula $C_9H_{14}O_5$; the compound is, moreover, identical in properties with the substance erroneously supposed by Nef to be ethyl acetylcarbintricarboxylate. Further proof that the compound obtained by the author is not ethyl acetylcarbintricarboxylate is afforded by the fact that even when the conditions are chosen so as to favour the formation of the last-named compound the principal product is, as before, ethyl carboxyethylacetoacetate.

Methyl carboxymethylacetoacetate, COOMe·CH:CMe·O·COOMe, is formed when methyl chlorocarbonate is treated with methyl sodacetoacetate in ethereal solution; it melts at 37—38°, and boils at 124—126° under a pressure of 19 mm., and at 224—226° with slight decomposition under the ordinary atmospheric pressure; it is insoluble in alkalis, and gives no colour reaction with ferric chloride. Molecular weight determinations in glacial acetic acid and in benzene solutions gave results agreeing with those required by a compound of the molecular formula $C_7H_{10}O_5$.

The ethereal salt of the composition $C_{10}H_{16}O_5$, obtained by treating ethyl sodiomethylacetoacetate with ethyl chlorocarbonate, is a colourless liquid of sp. gr. 1·085 at 15°, insoluble in alkalis; it boils at 136—139° under a pressure of 15 mm., that is to say, a few degrees higher than the compound obtained in like manner from ethyl acetoacetate; if the latter had the constitution assigned to it by Nef, the difference in boiling point would have been about 50° or 60° the other way.

A careful investigation of the interaction of ethyl chlorocarbonate and ethyl sodiomalonate has completely confirmed the statements of Conrad and Guthzeit on this subject; the sole product is ethyl methanetricarboxylate (m. p. 28°), the vapour density and molecular weight of which were determined by the usual methods; this ethereal salt has a distinctly acid character, and dissolves freely in dilute alkalis. F. S. K.

Action of Ethyl Cyanacetate on Organic Bases. By I. Guareschi (*Chem. Centr.*, 1892, i, 382—383; from *Atti. R. Accad. Sci. Torino*, **27**).—Ethyl cyanacetate reacts with ethylenediamine with development of heat, *dicyanacetylethylenediamine*,

$$C_2H_4(NH\cdot CO\cdot CH_2\cdot CN)_2,$$

and ethyl alcohol being formed. The mixture solidifies on cooling to a white, crystalline mass. Dicyanacetylethylenediamine is sparingly soluble in cold water, readily soluble in hot water and in alcohol, insoluble in ether. When strongly heated, it decomposes into ammonia, hydrogen cyanide, and an odour of coniine is emitted.

With pentamethylenediamine, ethyl cyanacetate forms the corresponding *dicyanacetylpentamethylenediamine*,

$$CH_2(CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot CN)_2.$$

It forms colourless needles melting at 135—136°. With benzylamine, *cyanacetylbenzylamine*, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$, is formed. It crystallises in beautiful, long, lustrous needles, melts at 124—124·5°, and boils at 339—340° with partial decomposition. It is soluble in hot water and alcohol, sparingly soluble in ether. This reaction of benzylamine with ethyl cyanacetate forms a means of separating it from aniline (see following abstract). A mixture of both bases is warmed gently with the cyanacetate for a few minutes, after which the mixture is distilled with steam, when the aniline passes over unchanged, whilst the residue contains the cyanacetylbenzylamine. The latter may then be boiled with potash, when benzylamine passes over. With piperidine, ethyl cyanacetate forms *cyanacetylpiperidine*, $C_5NH_{10}{\cdot}CO{\cdot}CH_2{\cdot}CN$, crystallising in large prisms, which melt at 88—89°. J. W. L.

Action of Ethyl Cyanacetate on Aniline. By E. Quenda (*Chem. Centr.*, 1892, i, 383; from *Atti R. Accad. Sci. Torino*, **27**).—Aniline reacts with ethyl cyanacetate only when heated. *Cyanacetylaniline* is first formed and then *malondianilide*, $CH_2(CO{\cdot}NHPh)_2$. The former, $NHPh{\cdot}CO{\cdot}CH_2{\cdot}CN$, is sparingly soluble in cold water, readily soluble in hot water and in alcohol, insoluble in ether; it melts at 198·5—200°, and volatilises at a higher temperature unchanged. It does not form salts with acids, and, when boiled with alkalis, it is decomposed into ammonia and aniline. J. W. L.

Constitution of Ethyl Acetoacetate and of the so-called Formyl Derivatives of Ethereal Salts and of Ketones. By L. Claisen (*Ber.*, **25**, 1776—1787).—Since it has been proved that ethyl acetoacetate yields two classes of derivatives, one of which must be regarded as derived from the ketonic ethereal salt $CH_2Ac{\cdot}COOEt$, whilst the other must be supposed to be derived from ethyl hydroxycrotonate, $OH{\cdot}CMe{:}CH{\cdot}COOEt$ (compare Nef, this vol., p. 140), there remain at the present time only two ways in which the constitution of ethyl acetoacetate can be determined, namely, by studying its physical properties and by comparing its chemical behaviour with that of compounds of known constitution.

Brühl (this vol., p. 583), from a determination of the molecular refraction of ethyl acetoacetate, concludes that at the ordinary temperature the compound must be represented by the ketone formula; this view is confirmed by the observations of Perkin (Proc., 1892, 100) on the molecular magnetic rotation of ethyl acetoacetate. Assuming that ethyl acetoacetate is a hydroxy-compound, the fact that it does not yield an acetyl derivative when heated with acetic anhydride or acetic chloride is remarkable. Further, if ethyl acetoacetate is ethyl hydroxycrotonate, it would probably show, to a certain extent, the same behaviour as ethyl salicylate, since both compounds contain the atomic complex $OH{\cdot}C{:}C{\cdot}COOEt$, but, as a matter of fact, the properties of the two compounds are quite different; as, however, the fact that in ethyl salicylate the atomic complex in question forms part of a closed chain, makes the analogy somewhat doubtful, the question can only be decided with certainty

by comparing the behaviour of ethyl acetoacetate with fatty compounds, such as the hydroxymethylene derivatives, which contain the atomic complex OH·C:C·CO—.

This comparison has shown that the behaviour of ethyl acetoacetate is so different from that of hydroxymethylenecamphor (Abstr., 1891, 574) and from that of the hydroxymethylene derivatives of ethyl phenylacetate, ethyl phenyl ketone, and deoxybenzoïn, that the constitution of the first named cannot be analogous to that of the hydroxy-compounds. The latter are converted by acetic chloride and by benzoic chloride into neutral acetates and benzoates just as readily as are the phenols; the benzoates are also formed when the sodium derivatives are suspended in ether and treated with benzoic chloride, and when the hydroxy-compounds are treated by Schotten-Baumann's method. When the sodium derivatives of the hydroxymethylene compounds are heated with ethyl iodide, alkyl derivatives of the constitution OEt·C:C·CO— are formed, with separation of sodium iodide; the same alkyl derivatives are obtained when the hydroxy-compounds are treated with phosphorus trichloride, and the chlorides obtained in this way decomposed with sodium ethoxide. These alkyl derivatives are hydrolysed by alcoholic potash and behave in this respect like the ethereal salts. On oxidation, the hydroxymethylene derivatives are decomposed in such a way that the :CH·OH group is replaced by an atom of oxygen.

A full account of these experiments will be published.

Since in many respects the hydroxymethylene derivatives are analogous to the isonitroso-compounds, it is possible that the former, like the latter, may exist in stereoisomeric forms; in the case of hydroxymethyleneacetone, for example, the two configurations would be represented by the formulæ $\begin{matrix}Ac\cdot C\cdot H\\ \|\\ OH\cdot C\cdot H\end{matrix}$ and $\begin{matrix}Ac\cdot C\cdot H\\ \|\\ H\cdot C\cdot OH\end{matrix}$. As a matter of fact, the benzoyl derivative of hydroxymethylenecamphor exists in two modifications, one of which can be converted into the other.

When the sodium derivative of hydroxymethyleneacetone is treated with benzoic chloride, there are formed two crystalline compounds, melting at 93° and 117° respectively; analyses of these two substances gave, in both cases, results agreeing with those required by a benzoyl derivative of the composition CHAc:CH·OBz; nevertheless, they are not isomeric. The compound of higher melting point can be obtained by heating the compound melting at 93° with excess of benzoic acid; it has, probably, the constitution $CH_2Ac\cdot CH(OBz)_2$, is insoluble in alkalis, and gives no coloration with ferric chloride.

When hydroxymethyleneacetone is treated with hydroxylamine, two isomeric isoxazoles are formed; they are both colourless liquids, having an intense pyridine-like smell. The one is *γ-methylisoxazole*, and boils at 118°. The isomeride boils at 122° and is *α-methylisoxazole;* this compound is converted into sodiocyanoacetone by sodium ethoxide. Cyanoacetone (compare Holtzwart, *J. pr. Chem.*, **39**, 237) is a colourless, unstable liquid, which readily undergoes polymerisation. F. S. K.

Action of Nitrous Acid on Ethyl Acetosuccinate and Diacetosuccinate. By R. Thal (*Ber.*, **25**, 1718—1727).—*Isonitrosolevulinic acid*, $COOH{\cdot}CH_2{\cdot}C(NOH){\cdot}COMe$, is obtained when a solution of ethyl acetosuccinate and potassium hydroxide (5 grams of each) in water (100 grams), after remaining at a moderately low temperature for 12 hours, is mixed with one of sodium nitrite (2 grams) in water (50 grams), the mixture being then cooled by ice, acidified with sulphuric acid, and quickly extracted with ether. The acid crystallises from ether in bunches of white needles, is readily soluble in alcohol, ether, and water, melts at 119° with the evolution of carbonic anhydride, whilst isonitrosomethylacetone distils over at 184—185°. It reduces Fehling's solution on warming, and, when kept, becomes black, being then insoluble in ether. The salts crystallise badly, the best being the *barium* salt, $(C_5H_6NO_4)_2Ba + 3H_2O$, which decomposes at 80°; the *phenylhydrazone* forms slender, silky needles, and melts at 152°. When an aqueous solution of the acid is mixed with hydroxylamine hydrochloride, and allowed to remain for some weeks, a brown, amorphous substance separates, whilst ether extracts a compound from the solution which crystallises from chloroform in leaflets, melts at 85°, and has one of the following constitutions, $NOH{:}CMe{\cdot}C\begin{matrix}N-O\\ |\\ CH_2{\cdot}CO\end{matrix}$ or $NOH{:}C\begin{matrix}CO-NMe\\ |\\ CH_2{\cdot}C\end{matrix}$. When isonitrosolevulinic acid is reduced with stannous chloride and hydrochloric acid, after adding an excess of concentrated potash, ether extracts tetramethylaldine; whilst, when the acid is allowed to remain in the cold with 20 times its weight of 15 per cent. sulphuric acid, an explosive compound, soluble in alkalis, is produced.

When ethyl diacetosuccinate is treated with nitrous acid in a similar manner to ethyl acetosuccinate, it gives two compounds, $C_2(NOH)_2(COMe)_2$ and $NOH{:}C(COMe){\cdot}CH_2{\cdot}COMe$; the former melts at 152·5° with decomposition, and the latter melts at 75° and boils at 185—188°. Ethyl β-methylacetosuccinate, on analogous treatment, yields a compound insoluble in all solvents with the exception of alkalis, which dissolve it with a yellow colour; it melts at 129—130° with the evolution of gas, and is probably methylisonitrosolevulinic anhydride, $COMe{\cdot}C\begin{matrix}N-O\\ |\\ CHMe{\cdot}C\end{matrix}$. A. R. L.

Hydrogenation of Closed Rings. By F. Stohmann and C. Kleber (*J. pr. Chem.* [2], **45**, 475—499).—See this vol., p. 1040.

Synthesis of Dihydrobenzene. By A. Baeyer (*Ber.*, **25**, 1840—1841).—The author has obtained dihydrobenzene by heating with quinoline the dibromohexamethylene obtained from quinitol (this vol., p. 833).

Dihydrobenzene is a liquid resembling benzene, has a characteristic penetrating odour, and boils at 81·5° (impure). The vapour at once turns paper moistened with permanganate brown. It combines with hydrogen bromide under the same conditions as dipentene, and forms a saturated *hydrobromide*. With bromine, it yields a beautifully

crystalline *tetrabromide*, which is reconverted into dihydrobenzene when treated with zinc-dust and acetic acid. With alcoholic sulphuric acid, it gives an intense blue coloration, and is converted into an oily condensation product. It dissolves in concentrated sulphuric acid with a red coloration. E. C. R.

Lignite Tar. By F. Heusler (*Ber.*, **25**, 1665—1678).—A quantity of the lighter portions of the distillate from lignite tar was fractionated after treatment with dilute acids and alkalis. On distillation at ordinary pressures, decomposition sets in at about 180°. The oil is readily attacked in the cold by potassium permanganate in dilute sulphuric acid solution. A quantity (1950 c.c.) of the oil boiling at 148—162° was treated with potassium permanganate (167 grams) in the cold until the action was over. On steam distillation, an oil (1208 grams) boiling at 130—165° was obtained; the largest fraction (328 grams) of this distilled at 145—150°. The lower boiling parts of the crude tar oil are acted on with explosive violence by nitric acid. After treatment with potassium permanganate, however, nitration proceeds quietly; the greater portion of the oil dissolves with evolution of gas, and on pouring the acid solution into water, a heavy oil separates which is partially soluble in soda. A considerable proportion, however, remains undissolved, and consists of nitro-derivatives of aromatic hydrocarbons.

On fractional bromination in the cold of the oil dissolved in ether, a product is obtained which may be separated by steam distillation into a light and a heavy oil. The lighter portion consists of bromo-derivatives of aromatic hydrocarbons.

Lignite tar oil is readily acted on by concentrated sulphuric acid with evolution of sulphurous anhydride. The oil (15 parts), if agitated first with a mixture of water (1 part) and concentrated sulphuric acid (2 parts) and then with a mixture ($4\frac{1}{2}$ parts) of water (1 part) and concentrated sulphuric acid (3 parts), yields an oil which, on steam distillation and subsequent fractionation, is found to be similar to that obtained by oxidation with permanganate and to have a strongly aromatic odour. The fraction of this oil, boiling at 80—93° was found, by nitration, to contain about 34 per cent. of benzene. The fraction boiling at 100—110° of the oil obtained by the treatment with permanganate, described above, was found by nitration to contain about 45 per cent. of toluene. Derivatives of metaxylene and mesitylene were also recognised among the products of nitration. The fraction boiling at 135—140° of the oil obtained by treatment with permanganate contained about 30 per cent. of aromatic hydrocarbons.

On nitration of the oil, a certain quantity was always unattacked; this consists of naphthenes, and the proportion increases as the boiling point of the oil rises, and varies from 14·5 per cent. in the fraction boiling at 90—100° to 33·3 per cent. in the part boiling at 300°.

No evidence of the presence of terpenes in the oil could be obtained on treating the oil by Wallach's methods. Indene and cumarone, also, could not be detected. The fraction boiling at

180—240° was found by treatment with picric acid to contain 4—5 per cent. of naphthalene. W. J. P.

Action of Iodoform on the Additive Product obtained from Sulphurous Anhydride and Sodium Phenoxide. By C. Schall and J. Uhl (*Ber.*, **25**, 1875—1901).—It has already been shown by Schall and Kopp (this vol., p. 970) that sulphurous anhydride and sodium phenoxide unite in molecular proportions forming the additive compound $NaSO_2 \cdot OPh$, which reacts with alkyl iodides forming the phenyl salts of alkylsulphonic acids. Benzyl chloride and carbonyl chloride act in a different manner, causing the evolution of sulphurous anhydride and forming benzyl phenyl ether and phenyl carbonate respectively. The authors then examined the action of iodoform in the hope of obtaining derivatives of the sulphonic acid, but the reaction proceeds in an entirely different manner to those mentioned above, yielding a substance of high molecular weight, which has the properties of a colouring matter.

The mixture of iodoform (1 mol.) and phenyl sodium sulphite (3 mols.) is heated in a sealed tube at 180°; the product contains, besides the above-mentioned colouring matter, considerable quantities of free iodine, sodium sulphate, sodium iodide, small quantities of water, carbon, methyl iodide, and phenyl methylsulphonate, sulphurous anhydride, and carbon monoxide being also evolved. To isolate the colouring matter, the product is treated with sodium thiosulphate to remove free iodine, the residue distilled in a current of steam, extracted with benzene, and, finally, recrystallised from alcohol with addition of water. It then forms odourless, microscopic plates, having a red to blackish-brown colour, or reddish-brown when in the form of powder; the authors, therefore, propose to term it *rubbadin* (from *ruber*, red, and *badius*, chestnut-brown) until its constitution shall be more exactly determined.

The analysis of the substance and the determination of its molecular weight by the boiling-point method lead to the formula $C_{44}H_{32}S_4O_8$; it sinters at 145°, commences to swell up and, apparently, to decompose at 160°, dissolves readily in alcohol, ethyl acetate, and phenol, sparingly in acetic acid, and is insoluble in other neutral solvents. Dilute soda and ammonia also dissolve it forming an intense Bordeaux-red solution, but the compound is reprecipitated unaltered by acids, or even by water from ammoniacal solution. In alcoholic or ammoniacal solutions it colours silk and wool a pale Bordeaux-red, and cotton a peculiar, pale yellowish-violet tint.

Diacetylrubbadin, $C_{44}H_{30}S_4O_8Ac_2$, is prepared by the action of an excess of acetic anhydride on rubbadin at 100°, and crystallises from chloroform on addition of light petroleum, and cooling strongly; it forms a greyish-yellow, crystalline powder which sinters at 155° and decomposes at a higher temperature without melting. On boiling in alcoholic solution, it undergoes decomposition, being resolved apparently into two acetyl derivatives, $C_{24}H_{16}S_2O_6Ac_2$ and $C_{20}H_{16}S_2O_2Ac_2$. With bromine it yields *hexabromodiacetylrubbadin*, $C_{44}H_{24}Br_6S_4O_8Ac_2$, which separates from ethyl acetate on addition of light petroleum as a fine, red, crystalline powder, and decomposes without melting above

300°. *Dimethylrubbadin*, $C_{44}H_{30}S_4O_8Me_2$, is obtained by boiling a solution of the colouring matter in alcoholic potash with a slight excess of methyl iodide; it is a dark, reddish-brown powder, and may be recrystallised from chloroform on addition of light petroleum, after which it sinters at 147° and decomposes at 210°.

When the solution of rubbadin in soda or acetic acid is treated with zinc-dust, 1 atom of sulphur is displaced by 2 atoms of hydrogen; the product separates in pale-red flakes, and can be crystallised from a mixture of ethyl acetate and light petroleum.

Concentrated nitric acid, freed from lower oxides by addition of carbamide, acts on an acetic acid solution of rubbadin, forming a *hexanitro*-compound $C_{44}H_{26}(NO_2)_6S_3O_8$, which contains 1 atom less sulphur than rubbadin, forms a red, crystalline powder, decomposing at 203°, and colours silk and wool pale yellow. When treated with reducing agents, it yields products which are insoluble in all solvents with the exception of phenol, and appear to consist of nitramido-derivatives.

Sulphuric acid acts on rubbadin with evolution of sulphurous anhydride and formation of other products which could not be isolated, whilst nitric acid at 100° yields picric acid and considerable quantities of sulphuric acid; on distillation with zinc-dust, it yields impure phenol. Dilute hydrochloric acid decomposes it at 200° with evolution of hydrogen sulphide and formation of phenol, and a new compound having the formula $C_{32}H_{20}S_2O_8$; the latter is a dark-red, crystalline powder, which decomposes above 300° without melting, dissolves readily in alcohol, ethyl acetate, and acetone, sparingly in acetic acid and ether; it also dissolves in concentrated soda, but scarcely in ammonia. When the alkaline solution is treated with methyl iodide, the *dimethyl* derivative, $C_{32}H_{18}S_2O_8Me_2$, is formed, which separates out in reddish-brown, lustrous plates, sinters at 200°, and decomposes on further heating. The *diacetyl* derivative

$$C_{32}H_{18}S_2O_8Ac_2,$$

is a yellowish-brown, crystalline powder, which sinters at 198°, and also decomposes on further heating; it combines with bromine to form the *tetrabromodiacetyl* derivative, $C_{32}H_{14}Br_4S_2O_8Ac_2$, which is a pale-red, crystalline powder.

When fused with soda and a little water, rubbadin yields phenol, a little salicylic acid, and *dihydroxydiphenyl sulphoxide*, $SO(C_6H_4{\cdot}OH)_2$. The latter forms a sandy, greyish-yellow powder which melts at 95°, is insoluble in benzene and light petroleum, readily soluble in ethyl alcohol, ether, and soda. Its *acetyl* derivative, $SO(C_6H_4{\cdot}OAc)_2$, is also a greyish-yellow powder, and melts at 108—109°. The same acetyl derivative is obtained from dihydroxydiphenyl sulphide by acetylation and oxidation with potassium permanganate, thus showing that the above constitution is correct. When dihydroxydiphenyl sulphoxide is heated with dilute hydrochloric acid at 200°, it is converted into a polymeride $(C_{12}H_{10}SO_3)_2$, which forms a reddish-brown, microcrystalline powder, and begins to melt at 188°.

The above results are insufficient to establish the exact constitution

of rubbadin, but the authors propose, provisionally, the following constitutional formula:—

$$HO\cdot C_6H_4\cdot CH{:}S<\begin{matrix}O\cdot O\cdot C_6H_4\\ O\text{—}C_6H_4\end{matrix}>S{:}S<\begin{matrix}C_6H_4\cdot O\\ C_6H_4\cdot O\end{matrix}>S<\begin{matrix}O\cdot C_6H_4\\ |\\ CH\cdot C_6H_4\cdot OH\end{matrix}$$

H. G. C.

Thymol. By F. Kehrmann (*Ber.*, **25**, 1662).—A polemical paper.

Orthophenylene Hydrogen Antimonite. By H. Causse (*Compt. rend.*, **114**, 1072—1074).—*Orthophenylene hydrogen antimonite*,

$$C_6H_4<\begin{matrix}O\\ O\end{matrix}>Sb\cdot OH,$$

is prepared by saturating an aqueous solution (200 c.c.) of catechol (20 grams) with sodium chloride at 50°; a neutral solution (100 c.c.) of antimonious chloride prepared by the author's method (see this vol., p. 413) is then added. On cooling, the antimonite crystallises out, and is separated after 24 hours, washed, and dried in the air. The substance does not melt; it is insoluble in most neutral solvents, but dissolves in alkalis and alkali carbonates, and in hydrochloric and sulphuric acids. Its solution in nitric acid soon decomposes with separation of antimonious oxide. It is decomposed by boiling with water or by treatment with hydrogen sulphide. On heating the salt (3 grams) with acetic anhydride (30 grams) in a closed vessel for four hours at 130°, diacetylcatechol is formed. Dibenzoylcatechol is obtained in a similar manner. W. J. P.

Paramidoalkylorthotoluidines. By A. Weinberg (*Ber.*, **25**, 1610—1614).—*Paramidoethylorthotoluidine* is prepared by the reduction of the corresponding nitroso-compound, and boils at 272° (corr.). The *sulphate*, $C_6H_2EtMe(NH_2)_2,H_2SO_4$, is deposited in large crystals on the addition of dilute sulphuric acid to the base dissolved in alcohol. By the action of nitrous acid on the base, a diazo-compound is formed. The *acetyl derivative* is obtained by heating the base with glacial acetic acid, and is amorphous; the salts are readily soluble. By the action of nitrous acid, a *nitrosamine* is formed as a yellow, viscid liquid.

On heating the acetyl derivative with ethyl bromide and alcohol in a sealed tube for 12 hours, *paracetamidodiethylorthotoluidine* is formed; it is a viscid liquid, and is purified by treatment with nitrous acid and ether; on heating with potash, *paramidodiethylorthotoluidine* is formed; this is a colourless liquid which does not undergo change on exposure to air, and boils at 260—261°. The *sulphate* crystallises in colourless prisms; the *hydrochloride* in small, lustrous plates. The *diazo-derivative* is pale yellow, and readily soluble. Paramidodiethylorthotoluidine does not yield thionine or indamine derivatives, neither could a thiosulphonic acid be obtained; this apparently points to an inner linkage between the amido- and alkyl-groups. That such is the case with paramidoethylorthotoluidine is shown by its yielding an indamine, a thionine, and a *thiosulphonic acid* which crystallises in lustrous prisms, and is almost insoluble in water. A comparison of the boiling points of aniline, ortho-, para-, and meta-toluidine, and of

the ethyl and diethyl substitution products shows that the boiling point rises with increasing molecular weight, except in the case of diethylorthotoluidine, which boils 9° lower than ethylorthotoluidine. The dialkylorthotoluidines do not condense with aldehydes, but the monoalkyl compounds readily combine to form methane derivatives.

J. B. T.

Oxalylorthamidophenyl Mercaptan, and Oxalylorthamido-α-naphthyl Mercaptan. By W. Lang (*Ber.*, **25**, 1902—1903).—When a mixture of aniline, glycerol, and sulphur is heated to the boiling point, hydrogen sulphide is evolved in quantity, the evolution continuing for 50—60 hours. If the product be then distilled, a yellow oil passes over far above 300° which quickly solidifies, and after recrystallisation from xylene forms pale-yellow needles, melts at 304°, and is identical with the oxalylorthamidophenyl mercaptan obtained by Hofmann from sulphur and acetanilide (Abstr., 1880, 885). If the aniline be replaced by α-naphthylamine, the oxalylorthamido-α-naphthyl mercaptan also described by Hofmann is formed, but the yield in both cases is much smaller than that obtained by the older method. The phenyl derivative may also be prepared by heating sulphur and ethylaniline at 200—300°.

H. G. C.

Dinitrosoazobenzene. By C. Wllgerodt (*J. pr. Chem.*, [2], **45**, 554—555).—The author complains that Kehrmann and Messinger (this vol., p. 889) have taken up an investigation which he had reserved. Even if it be granted that their experimental work is correct they are wrong in drawing the conclusion that "dinitrosoazobenzene" is nitrophenylazimidobenzene. A. G. B.

Action of Diazo-compounds on Oximes. By J. Mai (*Ber.*, **25**, 1685—1689).—The author continues his study of the action of diazo-compounds on oximes (see this vol., p. 163).

Paratoluidine (2·5 grams) is diazotised in hydrochloric acid solution and slowly added to an ice-cold aqueous solution of ethylaldoxime (3 grams) and potash (2 grams). The reaction is somewhat uncertain, an oily mass sometimes being formed; the normal product is a solid which is extracted with ether. On evaporation of the ethereal solution, a viscid mass is obtained which ultimately solidifies, and on crystallisation from light petroleum yields colourless leaves which melt at 86°, and decompose with evolution of gas at above 120°. This substance may have the constitution $C_6H_4Me{\cdot}NH{\cdot}N(O{\cdot}N{:}CHMe)_2$. It is sparingly soluble in ether, more so in alcohol, and separates unchanged from its solution in acetic acid.

The interaction of ethylaldoxime and diazobenzene chloride results in the formation of a substance which separates from light petroleum as an oil which ultimately solidifies and is deposited from ether as a solid which melts at 86° and decomposes with evolution of gas at 120°. Its constitution may be $NHPh{\cdot}N(ON{:}CHMe)_2$.

Paratoluidine (2 grams) and acetoxime (3 grams), when treated as described above, give a quantitative yield of a substance having

the composition $C_{13}H_{20}N_4O_2$, which crystallises from a mixture of alcohol and ether in scales melting with evolution of gas at 140—145°.

Similarly, diazobenzene chloride and acetoxime yield a compound of the composition $C_{12}H_{18}N_4O_2$, which crystallises from a mixture of alcohol and ether.

The two benzaldoximes react with diazobenzene chloride giving crystalline compounds of the composition $C_{20}H_{18}N_4O_2$, which melt with decomposition at 125°, and agree completely in their properties.

W. J. P.

Oximes. By A. Claus (*J. pr. Chem.*, [2], **45**, 556—560).—A reply to the recent paper by V. Meyer and Cathcart (this vol., p. 992; compare this vol., pp. 598, 985). A. G. B.

Parethoxyphenylhydrazine and Dimethylparethoxyphenylpyrazolone. By F. Stolz (*Ber.*, **25**, 1663—1665).—*Parethoxyphenylhydrazine*, $OEt{\cdot}C_6H_4{\cdot}N_2H_3$, is prepared by cautiously diazotising parethoxyaniline dissolved in concentrated hydrochloric acid, and subsequently reducing the cooled solution with stannous chloride and hydrochloric acid. It crystallises from benzene in lustrous leaflets, reduces Fehling's solution, melts at 74°, and is sparingly soluble in ether; the free base deliquesces and becomes dark on exposure to the air.

Parethoxyphenylmethylpyrazolone, $N\lessdot^{CMe\,--\,CH_2}_{N(C_6H_4{\cdot}OEt)}\!>CO$, separates as a crystalline mass when molecular proportions of the last described compound and ethyl acetoacetate are dissolved in toluene and the solution heated on the water-bath; it melts at 147°, and resembles pyrazolone in its behaviour. When heated at 100—120° with methyl iodide and wood spirit, *dimethylparethoxyphenylpyrazolone* (*parethoxyantipyrine*) $NMe\lessdot^{CMe=\!=CH}_{N(C_6H_4{\cdot}OEt)}\!>CO$, is produced; this crystallises in lustrous leaflets, melts at 90—91°, and resembles antipyrine in its general behaviour. A. R. L.

Paralkyloxy-derivatives of Phenylhydrazine, Hydracetine, and Antipyrine. By J. Altschul (*Ber.*, **25**, 1842—1854).—The author has been working on the same compounds as Stolz (preceding abstract) and claims priority. The preparation of parethoxyphenylhydrazine by V. Meyer's method, namely, by the action of stannous chloride and hydrochloric acid on the diazo-salt of parethoxyamidobenzene gives very bad results; the author has obtained good results by a modification of E. Fischer's method.

Sodium parethoxydiazobenzenesulphonate, $OEt{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_3Na$, is obtained by treating a mixture of parethoxyamidobenzene (100 grams), water (750 grams), and hydrochloric acid (sp. gr. = 1·19; 200 grams) with sodium nitrite (54 grams), dissolved in water (400 grams); when the diazotisation is complete, the mixture is poured into a mixture of sodium sulphite (400 grams), water (1600 grams), ice (500 grams), and sodium hydroxide (40° B., 120 grams). The diazosulphonate is thus obtained as a crystalline, yellow precipitate. That remaining in

the mother liquor is precipitated with salt. It crystallises from water in beautiful, yellow leaflets and thick, brownish-yellow prisms.

Sodium parethoxyphenylhydrazinesulphonate is obtained by gradually adding zinc dust (200 grams) to a solution of the above salt (400 grams) in water (2000 grams), and acetic acid (200 grams). On concentrating the filtrate, the greater part of the hydrazine sulphonate crystallises out; the rest is precipitated with salt. It crystallises in small, colourless prisms, is easily soluble in warm water, when damp quickly turns yellow, but remains unaltered when dry, and reduces Fehling's solution in the cold.

The corresponding methoxy-salts are obtained in a similar way. *Sodium paramethoxydiazobenzenesulphonate* forms yellow leaflets very similar to the ethoxy-salt. *Sodium paramethoxyphenylhydrazinesulphonate* crystallises in white needles.

When the above sodium hydrazinesulphonates are treated with concentrated hydrochloric acid with the object of converting them to the hydrazine hydrochlorides, decomposition takes place, and the properties characteristic of the hydrazine group are lost. The hydrazine hydrochlorides are easily obtained by treating them with alcoholic hydrogen chloride.

Parethoxyphenylhydrazine hydrochloride is obtained as follows:—A mixture of dry sodium paraethoxyphenylhydrazinesulphonate (100 grams), and 90 per cent. alcohol (600 grams) is heated to boiling in a reflux apparatus and mixed with hydrochloric acid (sp. gr. 1·19; 20 grams); after a short time the mixture is filtered hot; the filtrate cooled to 10° and mixed with a further quantity (350 grams) of hydrochloric acid. The semi-solid, crystalline mass so obtained is filtered and washed with alcohol. It crystallises from water or alcohol in colourless needles, is very easily soluble in water, less so in alcohol, decomposes when in a damp state, but is stable when dry. On adding ammonium oxalate to the aqueous solution, the *hydrazine oxalate* is precipitated in beautiful, colourless prisms.

Parethoxyphenylhydrazine is obtained by heating the hydrochloride with concentrated sodium hydroxide on the water-bath. It forms a bright-yellow, crystalline powder, melts at 74°, is distinctly soluble in cold water, easily in alcohol, sparingly so in ether, is very unstable, and soon decomposes into a brownish-red resin. It can be distilled in a vacuum, when it partially decomposes and the colourless distillate is a mixture of crystals (m. p. 74°) and a yellowish oil. When heated with aqueous mineral acids or with organic acids, it is quickly decomposed with formation of ammonia. On examining the alcoholic mother liquors obtained from crystallisation of the hydrochloride, the author separated parethoxyazobenzene, $N_2(C_6H_4{\cdot}OEt)_2$. When treated with glacial acetic acid at 100°, the mono- and di-acetyl compounds are obtained. *Monacetylparaethoxyphenylhydrazine* crystallises from water in colourless leaflets, from alcohol in lustrous prisms, melts at 141·5°, is soluble in 20 parts of boiling water and in 1 part of hot alcohol, and is sparingly soluble in cold water. It is distinguished from hydracetine by a characteristic colour reaction. The latter yields a colourless solution with sulphuric acid which goes

red on the addition of nitric acid. Monacetylparaethoxyphenylhydrazine dissolves in sulphuric acid with a blood-red coloration which changes to a beautiful yellowish-green on adding nitric acid. The *diacetyl compound* is obtained from the mother liquors of the monacetyl compound. It melts at 112—116° and forms colourless crystals similar to the monacetyl compound. Both compounds reduce Fehling's solution in the cold.

The corresponding methoxy-compounds are obtained in a similar way. *Paramethoxyphenylhydrazine* melts at 65°, and is more sparingly soluble in water and more easily so in ether than the ethoxy-compound. The *monacetyl compound* crystallises from water in colourless leaflets, melts at 133·5°, and gives the same colour reactions as the ethoxy-compound.

The decomposition of salts of hydrazinesulphonic acids by means of alcoholic hydrogen chloride may be used with advantage in other cases. The author has obtained phenylhydrazine by this method in a very pure state and from potassium parahydroxyphenylhydrazinesulphonate he obtained a compound which he believes to be parahydroxyphenylhydrazine.

Parethoxyphenylhydrazinesulphonic acid is obtained as follows:— The sodium salt (50 grams) is dissolved in warm water (200 grams), cooled to 40°, and mixed with 7 per cent. hydrochloric acid (100 grams). The liquid turns deep yellow, and after a short time solidifies to a crystalline magma. It is purified by washing with water. It leaves no ash on combustion, is easily soluble in alcohol, sparingly so in water, and is entirely decomposed on heating at 100°, and also by boiling with water and aqueous acids; the aqueous solution blues Congo-paper. On remaining, it quickly changes into *paradiethoxysulphophenylhydrazide*, $(OEt{\cdot}C_6H_4{\cdot}N_2H_2)_2SO_2$. The latter is undecomposed by heating at 100°, turns brown at a higher temperature, and decomposes at 130—140°. It is sparingly soluble in water, crystallises in white needles, is neutral, has strong reducing properties, and yields paraethoxyphenylhydrazine when treated with alcoholic hydrogen chloride, and subsequently with sodium hydroxide.

Ethyl acetoacetate reacts with parethoxyphenylhydrazine as described by Stolz (preceding abstract), and the author obtained parethoxyphenylmethylpyrazolone (m. p. 147°) and parethoxyphenyldimethylpyrazolone (m. p. 91°). The latter crystallises in colourless prisms about a centimetre long.

Parethoxyantipyrine salicylate is obtained by melting parethoxyantipyrine with the equivalent quantity of salicylic acid and a little alcohol. It crystallises from alcohol in beautiful, colourless prisms, and melts at 131°.

Paramethoxyphenyldimethylpyrazolone is very similar to the ethoxy-compound, and melts at 82°.

The author has prepared nitrophenylmethylpyrazolone from paranitrophenylhydrazine by the action of ethyl acetoacetate, and finds that it is identical with the nitro-compound obtained by nitrating phenylmethylpyrazolone. E. C. R.

Isomeric Oximes and Hydrazones. By A. Hantzsch (*Ber.*, **25**, 1692—1700).—This paper is purely polemical, being a reply to Claus (this vol., pp. 50, 598), who opposes stereochemical hypotheses. W. J. P.

Derivatives of Dibenzylcarbamic, Paraditolylcarbamic, and Benzylparatolylcarbamic Acids. By H. Hammerich (*Ber.*, **25**, 1819—1825).—*Dibenzylcarbamic chloride*, $N(CH_2Ph)_2 \cdot COCl$, is formed when carbonyl chloride is treated with dibenzylamine (2 mols.) in toluene solution; it is a yellow oil and decomposes on keeping.

Phenyldibenzylcarbamide, $C_{21}H_{20}N_2O$, prepared by treating the preceding compound with aniline in alcoholic solution, crystallises in small, lustrous needles, melts at 126—128°, and is soluble in hot alcohol, ether, benzene, and glacial acetic acid, but insoluble in water and light petroleum.

Paratolyldibenzylcarbamide, $C_{22}H_{22}N_2O$, crystallises in small, prismatic needles, melts at 168—169°, and is soluble in hot alcohol, benzene, and glacial acetic acid, but insoluble in ether, light petroleum, and water.

Tribenzylcarbamide, $C_{22}H_{22}N_2O$, crystallises in prisms, melts at 119—120°, and is soluble in benzene, ether, alcohol, and glacial acetic acid.

Tetrabenzylcarbamide, $C_{29}H_{28}N_2O$, crystallises in hexagonal prisms, dissolves freely in ether, benzene, alcohol, and glacial acetic acid, and melts at 85°.

Isobutyldibenzylcarbamide, $C_{19}H_{24}N_2O$, crystallises in small, prismatic needles, melts at 108—109°, and is readily soluble in ether, benzene, glacial acetic acid, and warm alcohol.

Paraditolylcarbamic chloride, $N(C_6H_4Me)_2 \cdot COCl$, crystallises in prismatic needles, melts at 102—103·5°, and is very readily soluble in ether and benzene, but more sparingly in glacial acetic acid, alcohol, and light petroleum.

Phenylparaditolylcarbamide, $C_{21}H_{20}N_2O$, melts at 135—136°, crystallises in prismatic needles, and is soluble in alcohol, benzene, ether, and glacial acetic acid.

Triparatolylcarbamide, $C_{22}H_{22}N_2O$, crystallises in prismatic needles, melts at 189°, and is insoluble in ether, light petroleum, and water, but soluble in warm benzene, glacial acetic acid, and alcohol.

Benzylparaditolylcarbamide, $C_{22}H_{22}N_2O$, melts at 136—137°; *tetraparatolylcarbamide*, $C_{29}H_{28}N_2O$, at 78—80·5°; and *isobutylparaditolylcarbamide*, $C_{19}H_{24}N_2O$, at 118—119°; they are all crystalline compounds soluble in alcohol, ether, benzene, and glacial acetic acid.

Benzylparatolylcarbamic chloride, $CH_2Ph \cdot N(C_6H_4Me) \cdot COCl$, is a dark brown oil.

Phenylbenzylparatolylcarbamide, $C_{21}H_{20}N_2O$, melts at 111—113°, *paraditolylbenzylcarbamide*, $C_{22}H_{22}N_2O$, at 115°, and *dibenzylparatolylcarbamide*, $C_{22}H_{22}N_2O$, at 83—85°; they are all crystalline compounds soluble in ether, alcohol, benzene, and glacial acetic acid.

Dibenzylditolylcarbamide, $C_{29}H_{28}N_2O$, separates from light petroleum in crystals, melts at 91—93°, and is soluble in alcohol, benzene, glacial acetic acid, and ether.

Isobutylbenzylparatolylcarbamide, $C_{19}H_{24}N_2O$, separates from light petroleum in crystals melting at 41°.

Ethyl dibenzylcarbamate, $C_{17}H_{19}NO_2$, is formed when dibenzylcarbamic chloride is heated with an alcoholic solution of sodium ethoxide; it is a yellowish liquid and cannot be distilled.

Ethyl paraditolylcarbamate crystallises from alcohol in well-defined, rhombic plates, melts at 60—62°, and dissolves freely in alcohol, benzene, ether, glacial acetic acid, and boiling light petroleum.

F. S. K.

Tetrabenzyloxamide and Tetraparatolyloxamide. By H. Hammerich (*Ber.*, **25**, 1825—1826).—*Tetrabenzyloxamide*,

$$N(CH_2Ph)_2\cdot CO\cdot CO\cdot N(CH_2Ph)_2,$$

prepared by treating dibenzylcarbamic chloride (compare preceding abstract) with sodium in ethereal solution, crystallises from alcohol in prismatic needles, melts at 127—128°, and is soluble in ether, benzene, and glacial acetic acid.

Tetraparatolyloxamide, $C_{30}H_{28}N_2O_2$, crystallises in small, lustrous plates, melts at 100—101·5°, and is soluble in benzene, alcohol, ether, glacial acetic acid, and light petroleum, but insoluble in water.

F. S. K.

Action of Silver Cyanide on Dibenzylchlorocarbamide and Paraditolylchlorocarbamide. By H. Hammerich (*Ber.*, **25**, 1827—1829).—*Dibenzylcyanocarbamide argentocyanide*,

$$N(CH_2Ph)_2\cdot CO\cdot CN,AgCN,$$

is obtained by heating dibenzylchlorocarbamide dissolved in alcohol with excess of silver cyanide in a reflux apparatus for 4 to 8 hours. The precipitate of silver chloride is filtered off and the filtrate evaporated to crystallisation. It crystallises in small, prismatic needles, melts at 165—167°, is soluble in alcohol, insoluble in ether, benzene, acetic acid, and light petroleum, and blackens on exposure to light.

Paraditolylcyanocarbamide diargentocyanide,

$$N(C_6H_4Me)_2\cdot CO\cdot CN,2AgCN,$$

is obtained in a similar way to the preceding compound. It crystallises in small, prismatic needles, begins to melt at 103°, gradually decomposes at higher temperatures, and blackens on exposure to light.

The author was unable to obtain an analogous compound from benzylparatolylchlorocarbamide.

E. C. R.

Aromatic Phosphino-compounds, RPO_2. By A. Michaelis and F. Rothe (*Ber.*, **25**, 1747—1752).—*Phosphinobenzene*, $Ph\cdot PO_2$, is obtained when dry phenylphosphinic acid (m. p. 158°; 7 grams) is heated in a reflux apparatus with the chloride of the same acid, $Ph\cdot POCl_2$ (12 grams), until the evolution of hydrogen chloride ceases. The product is washed with dry cold benzene, dissolved in hot benzene, and the concentrated solution cooled to its solidifying point. On now cautiously thawing the benzene and decanting it, the com-

pound remains, and is dried first in a current of carbonic anhydride at 70°, and subsequently in a desiccator. It is a white, crystalline powder, melts at 100°, is readily soluble in benzene, and when exposed to moist air is converted into phenylphosphinic acid, thus behaving as an anhydride of the latter.

Paraphosphinotoluene, $C_6H_4Me{\cdot}PO_2$, is prepared from paratolylphosphinic acid (m. p. 189°) and its chloride in the same manner as the benzene derivative, which it resembles; it melts at 101°.

Phosphino-ψ-cumene, $C_6H_2Me_3{\cdot}PO_2$, is obtained from *ψ-cumylphosphinic acid* (m. p. 212°), which will be described in a subsequent paper, and its chloride. It separates from benzene in small, well-formed, rhombic leaflets, melts at 216°, and is sparingly soluble in cold benzene, very easily in chloroform, and insoluble in light petroleum. It does not absorb water so readily as do the two first-mentioned analogues.

The phosphino-compounds are also obtained when the substituted phosphorous acids are heated with phosphoric chloride; this method does not, however, give such good results as the alternative one. The remainder of the paper is devoted to a comparison of the phosphorus and arsenic analogues of nitrobenzene, azobenzene, and aniline. A. R. L.

Ethylnitroketone and Acetylnitroketone from Camphosulphophenols. By P. Cazeneuve (*Compt. rend.*, **114**, 1012—1014). —The nitroketone derived from the camphosulphophenols (this vol., 999) seems to be a nitroketone of a propylbenzene dihydride ($NO_2 : H_2 : O : Pr = 1 : 2 : 3 : 4$), the methyl of the paracymene nucleus of camphor having disappeared on the formation of a methyl camphophenolsulphone and its isomeride.

The potassium salt of the nitroketone, when heated with excess of ethyl iodide at 130° for an hour, yields an ethyl derivative, $NO_2{\cdot}C_9H_{10}OEt$. It is a yellow, syrupy liquid, insoluble in water, but miscible with alcohol or ether, and it explodes if heated rapidly above 200°. When treated with a cold alcoholic solution of sodium ethoxide, it yields immediately an alkaline salt, $NO_2{\cdot}C_9H_{10}ONa$, with liberation of ether.

The carefully-dried potassium salt reacts rapidly with acetic chloride. The latter is added gradually until the red colour changes to yellow, showing that the reaction is complete, and the product is washed, first with water, then with water containing alkali, and is finally crystallised from alcohol, from which it separates in large, greenish-yellow, tabular hexagons. This product is the acetyl derivative, $NO_2{\cdot}C_9H_{10}OAc$; it melts at 65°, remains in superfusion even at the ordinary temperature, and explodes if heated above 250°. When treated with an alcoholic solution of sodium ethoxide, it yields ethyl acetate and the sodium derivative of the nitroketone.

Although the ethyl and acetyl derivatives are somewhat unstable, it still seems necessary to assume the existence of the grouping $NO_2 : H_2 : O = 1 : 2 : 3$. The difference between the acidic function of the CH_2 group in this nitroketone and in acetylacetone is probably due to the fact that in the latter the CH_2 group is connected with

two carbonyl groups, and not with one nitro-group and one carbonyl group. C. H. B.

Phenylanthranilic Acid and Acridone. By C. Graebe and K. Lagodzinski (*Ber.*, **25**, 1733—1736).—Phenylanthranilic acid, $COOH{\cdot}C_6H_4{\cdot}NHPh$ [1 : 2], is prepared by reducing Schöpff's meta-nitrorthanilidobenzoic acid (Abstr., 1891, 304) with tin and hydrochloric acid and eliminating the amido-group by the diazo-reaction. It forms a compound with concentrated hydrochloric acid, which is decomposed on addition of water, and, when nitric acid is added to its solution in a little concentrated hydrochloric acid, an intense, violet coloration is produced; it melts at 181° (corr.), which value is not in agreement with that of Claus and Nicolaysen (Abstr., 1886, 68); Claus is, however, resuming its study.

When phenylanthranilic acid is heated at 100° with concentrated sulphuric acid for 1—2 hours, acridone, $C_6H_4{<}\overset{CO}{NH}{>}C_6H_4$, which is perhaps identical with the compound obtained by Graebe and Caro by oxidising acridine (Abstr., 1880, 399), is formed; it crystallises in stout, yellow needles, melts at 350°, volatilising at a higher temperature without decomposition, and dissolves somewhat readily in hot alcohol or glacial acetic acid, its solution having a yellow colour and a bluish fluorescence; it also dissolves in concentrated hydrochloric acid on warming, but is insoluble in aqueous alkalis. It gives Decker's methylacridone (this vol., p. 881) on methylation, and, when heated with zinc-dust, it is quantitatively converted into acridine.

A. R. L.

Condensation of Ethyl Cyanacetate and Benzaldehyde: Ethyl α-Cyanocinnamate. By J. T. Carrick (*J. pr. Chem.* [2], **45**, 500—515).—The author has already shown that this condensation takes place at the ordinary temperature in the presence of sodium ethoxide (Abstr., 1890, 1270), the product of the reaction being *ethyl α-cyanocinnamate*. The best yield is 80 per cent. of the calculated quantity, the conditions being those already given (*loc. cit.*). The same product was obtained in very small quantity when benzaldehyde (5 grams), acetic anhydride (20 grams), and ethyl cyanacetate (5 grams) were heated together in a sealed tube at 150—160°.

Ethyl α-cyanocinnamate melts at 50°, and boils with decomposition about 360°; it dissolves very easily in hot alcohol, in 8—9 parts at the ordinary temperature, and very slightly below 0°; water does not dissolve it at all, but ether, chloroform, benzene, and glacial acetic acid do so easily; it is very volatile with alcohol vapour and with steam. Dilute aqueous alkalis readily decompose it into benzaldehyde and ethyl cyanacetate, which further yields malonic acid, ammonia, and, finally, acetic acid and carbonic anhydride; but with hot water and cold, even concentrated, acids, it is very stable. When heated with concentrated hydrochloric acid in a sealed tube, it is converted into carbonic anhydride, benzaldehyde, and malonic acid. It is unattacked by hot glacial acetic acid, and only decomposed to a slight extent by a mixture of glacial acetic acid and acetic anhydride

in a sealed tube at 150—160°. It is not attacked by bromine, or by hydrogen, either from zinc-dust or sodium amalgam, in glacial acetic acid. Its molecular weight, as determined by Raoult and Beckmann's method, corresponds with the formula $C_{12}H_{11}NO_2$.

α-Cyanocinnamic acid, $C_{10}H_7NO_2$, melts at 178°, and is prepared from the ethyl salt by saponifying it with alcoholic potash, dissolving the *potassium* salt in warm water, cooling, and adding acetic acid; the white precipitate thus thrown down is the hydrogen potassium salt, and yields the acid when dissolved in warm water and decomposed by hydrochloric acid. The molecular weight of the acid was determined. The *hydrogen potassium* salt, $KC_{20}H_{13}N_2O_4$, crystallises in long needles, melts at 240° with decomposition, and is soluble in water, but not in ether; when silver nitrate is added to its alcoholic solution, the *silver potassium* salt, $KAgC_{20}H_{12}N_2O_4$, is precipitated in long, silky needles, contrasting with the *normal silver* salt, which is amorphous. The *normal ammonium* salt, $NH_4{\cdot}C_{10}H_6NO_2$, is obtained when alcoholic ammonia is added to an ethereal solution of the acid, and the *hydrogen ammonium* salt when this is dissolved in water, cooled to 0°, and decomposed with dilute acetic acid; the latter salt melts with decomposition at 210°. The *normal barium* salt,

$$(C_{10}H_6NO_2)_2Ba + H_2O,$$

the *normal copper* salt, the *normal lead* salt (with 4 mols. H_2O), and an *aniline* salt, $C_{10}H_7NO_2{\cdot}NH_2Ph$, were also prepared. By heating the potassium salt with ethyl bromide at 140—150°, it was reconverted into the ethyl salt (m. p. 50°).

When the ethyl salt is dissolved in alcoholic ammonia, there separates, after a time, a crystalline compound which melts at 168°, and is converted into an oil, having the odour of benzaldehyde, when evaporated with ammonia. This crystalline compound appears to be *ethyl cyanocinnamamate*, $CHPh{:}C(CN){\cdot}COOEt,CHPh{:}C(CN){\cdot}CONH_2$; it is insoluble in water and requires 270 parts of ether and 50—60 parts of hot alcohol to dissolve it; chloroform dissolves it easily, while benzene, glacial acetic acid, and strong sulphuric acid separate benzaldehyde from it; alkalis decompose it immediately. When methylamine is substituted for ammonia, the resulting substance has the formula $CHPh{:}C(CN){\cdot}COOEt,CHPh{:}C(CN){\cdot}CO{\cdot}NHMe$, but appears to be a mixture of two isomerides, one of which dissolves in glacial acetic acid and melts about 180° with decomposition, whilst the other is insoluble in this solvent and melts about 157° with decomposition. Attempts to obtain normal cyanocinnamamide failed.

When the ethyl salt is kept in concentrated aqueous ammonia for 24 hours, it becomes converted into a yellow oil which gradually dissolves in the liquid yielding an insoluble precipitate; this precipitate behaves as a very feeble base, and is easily soluble only in chloroform and concentrated mineral acids; it melts at 194°. Another new compound is precipitated by acidifying the ammoniacal solution; it dissolves in chloroform, and melts with decomposition between 175° and 200°.

The oil obtained as a bye-product in the preparation of ethyl

cyanocinnamate (Abstr., 1890, 1270) solidifies gradually, and then has the same melting point as the ethyl salt; it also contains the same percentage of nitrogen and behaves similarly to reagents. The author, therefore, concludes that it is a geometrical isomeride of the ethyl salt (compare Fiquet, *Bull. Soc. Chim.* [3], **7**, 11).

A. G. B.

Mandelic Acid and its Nitrile. By H. A. Michaël and J. Jeanprêtre (*Ber.*, **25**, 1678—1684).—Attempts were made, with negative results, to prepare a sodium derivative of phenylhydroxyacetonitrile corresponding with that yielded by phenylacetonitrile (V. Meyer, Abstr., 1889, 596), in order that by its interaction with ethyl iodide, phenylethoxyacetonitrile might be obtained.

Phenylchloracetonitrile is prepared by slowly adding phenylhydroxyacetonitrile to a strongly cooled solution of phosphorus pentachloride (1 part) in benzene (3 parts). The solution is finally heated on the water-bath, cooled, and poured on to ice. On evaporation of the benzene solution, the nitrile remains as an oil which, after fractional distillation under reduced pressure, boils at 131—133° at ordinary pressures. It is a colourless, strongly refractive liquid, and its vapour has a very irritating effect on the eyes and lungs. On hydrolysis with concentrated hydrochloric acid in a sealed tube at 100°, it readily yields phenylchloracetic acid and phenylchloracetamide. On treating the nitrile with alcoholic sodium ethoxide, sodium chloride is precipitated, and dicyanostilbene remains in solution. This is a good method for the preparation of dicyanostilbene as the yield is large. On heating an ethereal solution of phenylchloracetonitrile (1 mol.) with aniline (2 mols.) for some time, phenylanilidoacetonitrile is obtained.

Phenylhydroxyacetonitrile (1 mol.) is quantitatively converted into an *acetyl* derivative, $C_{10}H_{10}O_3N$, on heating with acetic anhydride (1 mol.) for three hours in a reflux apparatus. On distillation under reduced pressure, the acetyl derivative is obtained as a colourless, viscid oil, which boils at 152° under 25 mm. pressure. On slowly pouring an ethereal solution of this compound into ether containing sodium in suspension, a solid substance containing sodium separates. This is treated with dilute sulphuric acid, and leaves a residue of benzoïn, whilst a compound which crystallises from alcohol in small, tabular crystals, and melts at 115°, goes into solution. The latter substance was not analysed.

The authors were unable to prepare the mandelamide melting at 190°, described by Biedermann (this vol., p. 473), but obtained in its place a substance melting at 132°. By the action of fuming hydrochloric acid on phenylhydroxyacetonitrile, Tiemann and Friedländer (*Ber.*, **4**, 1967) obtained a compound melting at 194°, and having the composition $C_{15}H_{13}O_2N$. The authors have prepared this substance by heating the mandelamide which melts at 132° with the equivalent proportion of benzaldehyde for two hours at 130°. This compound yields no nitroso-compound, but on heating with acetic anhydride gives an *acetyl* derivative, $C_{17}H_{15}O_3N$, which crystallises from alcohol in beautiful prisms and melts at 123°. The constitution of the substance melting at 194° is therefore OH·CHPh·CO·N:CHPh.

The authors were unable to prepare ethyl mandelate melting at 79° as described by Naquet and Louguinine (*Bull. Soc. Chim.*, **5**, 255), but obtained an ethyl salt which crystallises in silky needles, melts at 34°, and boils without decomposition at 250°. They therefore conclude that Naquet and Louguinine were dealing with some other derivative of mandelic acid. W. J. P.

Ethoxyphenylsulphonic Acids. By G. Lagai (*Ber.*, **25**, 1836—1839; see also Abstr., 1891, 310).—*Lead metethoxyphenylsulphonate*, $(OEt{\cdot}C_6H_4{\cdot}SO_3)_2Pb + 2\frac{1}{2}H_2O$, crystallises in colourless, lustrous leaflets, and deliquesces in the air. The *aniline salt* is obtained by the action of aniline sulphate on the barium salt, and forms pale-yellow needles. *Metethoxyphenylsulphanilide*, obtained by heating the sulphochloride with aniline, crystallises from alcohol in lustrous, colourless needles or plates, melts at 88°, and is easily soluble in ether, alcohol, and benzene, sparingly so in water. *Ethyl metethoxyphenylsulphonate*, a pale-yellow, oily liquid, is volatile with steam, and, on distillation, is decomposed with formation of a compound having an odour resembling that of mercaptan.

Parethoxyphenylsulphonic acid was prepared by heating potassium paraphenolsulphonate, potassium hydroxide, ethyl bromide, and alcohol, for 12 hours at 100—110°. It was also prepared by sulphonating ethoxybenzene with twice the weight of concentrated sulphuric acid at 100°; in the latter case a small quantity of the ortho-acid is formed. The *sulphochloride* crystallises from ether in hard, colourless prisms, or thick plates, melts at 36·5°, and is very easily soluble in alcohol and ether. The *sulphonamide* crystallises from alcohol in colourless plates, and from water in long, white needles, and melts at 149°. The *sulphanilide* crystallises from dilute alcohol in beautiful, silky needles, and melts at 84°. *Aniline parethoxyphenylsulphonate* crystallises from water in lustrous, pale-yellow needles, and melts at 224° with decomposition. *Parethoxyphenylsulphonic acid* separates from concentrated aqueous solution in feathery crystals. The *hydrosulphide*, a colourless, highly refractive liquid, boils at 232·5°, has an unpleasant odour, is volatile with steam, and with concentrated sulphuric acid gives a yellow coloration, which changes successively to olive-green and dark-blue. With metallic sodium, the hydrosulphide yields a compound which crystallises from absolute alcohol in massive, colourless prisms, and melts at 45°. With mercuric chloride, it yields a compound of the formula $OEt{\cdot}C_6H_4{\cdot}S{\cdot}HgCl$, which crystallises from alcohol, in which it is sparingly soluble, in thin, silvery leaflets, and melts at 178°.

Orthoethoxyphenylsulphonic acid is obtained in small quantities by sulphonating ethoxybenzene, and is separated from the para-acid by means of the barium salt, which is extremely soluble in water. It could not be obtained crystalline. The *sulphochloride* forms a syrupy liquid. The *sulphonamide* crystallises from water in feathery needles, melts at 142°, and is easily soluble in ether, less so in alcohol, and sparingly in water.

According to Moody (Proc., 1892, 90), the orthosulphonic acid is not formed by the sulphonation of ethoxybenzene. E. C. R.

Oxidation Products of Mercapturic Acids. By G. König (*Zeit. physiol. Chem.*, 16, 525—551; compare Baumann and Preusse, Abstr., 1879, 803; Jaffé, *ibid.*, 796; Baumann, Abstr., 1884, 1382 and 1395). — *αα-Acetamidoparachlorophenylsulphonepropionic acid*, $COOH{\cdot}CMe(SO_2{\cdot}C_6H_4Cl){\cdot}NHAc$, is prepared by dissolving chlorophenylmercapturic acid (10 grams) in normal potassium hydroxide solution (38·5 c.c.), diluting to 2 litres, and adding potassium permanganate (8 grams) in 5 per cent. solution; the mixture is allowed to remain for a day, and the filtrate subsequently neutralised with dilute sulphuric acid, evaporated to a small volume, poured into alcohol, and after filtering off the potassium sulphate, and evaporating the remainder of the alcohol from the filtrate, the residue is dissolved in a small quantity of water and strongly acidified with hydrochloric acid, when the acid separates; it is recrystallised from boiling water, and forms long, thin, colourless prisms or rhombic plates, melts at 177° with decomposition, and is soluble in 45 parts of boiling water and 700 parts of cold, readily soluble in boiling alcohol, sparingly so in the cold liquid, but insoluble in ether, benzene, and chloroform. It gives a blue and a brownish colour respectively when warmed with concentrated sulphuric acid or acetic anhydride, and is a strong, monobasic acid. The *barium* salt crystallises with $1\frac{1}{2}$ mol. H_2O in white, microscopic needles, which are deliquescent, and the *silver* salt forms small, felted needles, which blacken in the light; the salts of the heavy metals are mostly amorphous. The *ethyl* salt crystallises in small, prismatic needles, melts at 165° with decomposition, and is sparingly soluble in cold water, readily in ether, chloroform, and alcohol; it gives no coloration on warming with concentrated sulphuric acid.

αα-Acetamidoparabromophenylsulphonepropionic acid is obtained from bromophenylmercapturic acid in the same way as the chloro-derivative; it crystallises from hot water in colourless prisms, melts at 170—171°, is sparingly soluble in cold water, readily so in alcohol, and gives, with concentrated sulphuric acid, a blue coloration having a greenish shade. The *barium* salt forms silky needles containing 4 mols. H_2O.

αα-Acetamidoparaiodophenylsulphonepropionic acid, prepared from iodophenylmercapturic acid, is much more readily soluble in water than the other halogen derivatives; it separates from concentrated solutions in boiling water in felted needles an inch in length, and melts at 169—170°.

Baumann having shown (*loc. cit.*) that when halogen benzenes are administered to dogs, compounds are found in the urine which yield halogen mercapturic acids on treatment with dilute mineral acids, it seemed probable that the corresponding halogen free compound would occur in the urine when benzene itself was administered; experiments in this direction, however, led to negative results.

αα-Acetamidophenylsulphonepropionic acid,

$$COOH{\cdot}CMe(SO_2Ph){\cdot}NHAc,$$

is obtained by oxidising phenylmercapturic acid (m. p. 140°) or by reducing the preceding halogenated acids; it crystallises from hot

water in small, pointed crystals, melts at 183°, decomposes at a higher temperature, is sparingly soluble in cold water or alcohol, and insoluble in ether, chloroform, and benzene; it gives a brownish-red coloration with concentrated sulphuric acid. The *barium* salt crystallises in small, microscopic needles, containing $\frac{1}{2}$ mol. H_2O; the *silver* salt forms small, anhydrous needles, and is readily soluble in water, ammonia, and nitric acid.

α-Amidoparachlorophenylsulphonepropionic acid,

$$COOH{\cdot}CMe(SO_2{\cdot}C_6H_4Cl){\cdot}NH_2,$$

is prepared by boiling the corresponding acetamido-derivative (m. p. 177°) with dilute (1 to 2) sulphuric acid in a reflux apparatus for about 10 minutes, neutralising with ammonia, and adding an excess of ammonium carbonate, when it separates; it crystallises from boiling water in nacreous leaflets, melts at 156°, requires 1400 parts of cold water for dissolution, being insoluble in boiling alcohol, ether, chloroform, and benzene, and has both acidic and basic properties. It dissolves in concentrated sulphuric acid on warming with the production of a violet solution, and gives the acetamido-derivative on acetylation. The corresponding *bromo*-compound resembles the chloro-derivative; it melts at 163—164°, and gives a reddish-brown solution on warming with concentrated sulphuric acid.

The *hydantoic acid*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_9H_8ClSO_4$, is formed when α-amidoparachlorophenylsulphonepropionic acid (1 gram) is suspended in water (20 c.c.) and moderately heated with potassium carbimide (4 grams); it crystallises from boiling water in stellate groups of small needles, melts at 173—174° with decomposition, and is readily soluble in hot water and alcohol, but insoluble in ether and chloroform; it gives a blue coloration on warming with concentrated sulphuric acid, and undergoes violent oxidation with nitric acid.

When either α-amidoparachlorophenylsulphonepropionic acid or the corresponding acetamido-derivative is boiled with alkalis, it yields ammonia, pyruvic acid, and parachlorobenzenesulphinic acid. The bromo-derivatives behave in the same manner, and *parabromobenzenesulphinic acid* obtained from them crystallises in long, prismatic needles, melts at 103°, and dissolves in concentrated sulphuric acid on warming, with the production of a blue coloration. It is to be noted that although the mercapturic acids, which are acetamido-compounds, yield sulphones on oxidation, this is not the case with the corresponding amido-derivatives.

Parachlorophenylsulphonehydroxypropionic acid,

$$COOH{\cdot}CMe(SO_2{\cdot}C_6H_4Cl){\cdot}OH,$$

is prepared by dissolving the amidoparachlorophenylsulphonepropionic acid (2 grams) in normal sulphuric acid (20 c.c.) and water (200 c.c.), warming, to the warm solution adding sodium nitrite (0·8 gram), dissolved in water (20 c.c.) and extracting with ether. It crystallises in small, colourless, stellate groups of prisms, melts at 155—156° with decomposition, gives a brown colour when warmed with concentrated sulphuric acid, and is soluble in water, alcohol, and ether;

its salts are easily soluble in water, and do not crystallise readily. When the hydroxy-compound is boiled with alkalis, and the solution subsequently acidified, the *compound* $[COOH\cdot CMe\cdot(SO_2\cdot C_6H_4Cl)]_2O$ is precipitated; it melts at 153°. A. R. L.

Toluic Sulphinide ("**Methylsaccharin**"). By O. Weber (*Ber.*, **25**, 1737—1745).—*Toluic sulphinide*, $C_6H_3{}^{1}Me{}^{3}\langle{}^{SO_2}_{CO}{}^{4}\rangle NH$, prepared from 1 : 4 : 3-amidotoluenesulphonic acid, according to German Patent 48583 (*Ber.*, **22**, Ref. 719), melts at 246°; the *silver* salt is obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt; the ethyl and methyl salts melt at 106° and 153° respectively. When the imide is dissolved in water (3 parts), heated at 80° on the water-bath with 7 per cent. potassium hypochlorite solution (10 parts) for some minutes, and, when cold, glacial acetic acid added to the solution, 1 : 4 : 3-amidotoluenesulphonic acid is precipitated. Commercial benzoic sulphinide ("saccharin"), not being a homogeneous compound, gives a mixture when similarly treated.

4 : 1 : 3-Sulphamidotoluic acid, $COOH\cdot C_6H_3Me\cdot SO_2NH_2$, is formed by boiling toluic sulphinide with water; it separates in faintly yellowish crystals, melts at 185°, and is sparingly soluble in the usual organic solvents. The *barium* salt crystallises with 2 mols. H_2O in colourless rosettes; the *ethyl* salt melts at 95°, and the *methyl* salt at 145°. On heating the acid at 210—220°, a sublimate of toluic sulphinide is obtained; whilst sulphoterephthalic acid, giving a potassium salt agreeing with that described by Hall and Remsen (Abstr., 1880, 257), is formed by oxidising it in acid solution, and terephthalic sulphinide on oxidising it in alkaline solution. The latter was found to melt at 284° instead of 297—299°, as stated by Noyes and Walker (Abstr., 1887, 728). When toluic sulphinide is twice evaporated on the water-bath with dilute hydrochloric acid, the ammonium salt, $COOH\cdot C_6H_3Me\cdot SO_3NH_4$ [4 : 3 : 1], is obtained; the corresponding acid (m. p. 181—182°) is described by Fittica (this Journal, 1874, 1166); the anhydride, $C_6H_3Me\langle{}^{CO}_{SO_2}\rangle O$, melts at 70°. When the anhydride is dissolved in dry benzene and dry ammonia led through, an *ammonium* salt, $CONH_2\cdot C_6H_3Me\cdot SO_3NH_4$, is produced, and when the silver salt corresponding with this is dissolved in water, and a current of hydrogen sulphide passed through, the *acid*,

$$CONH_2\cdot C_6H_3Me\cdot SO_3H,$$

melting at 186°, is obtained.

Hydroxytoluic acid [OH : Me : COOH = 3 : 1 : 4] is formed on fusing the above-mentioned sulphoterephthalic acid with potash (3 parts) at 200—300°; it furnishes the *phenyl* salt (*homosalol*) on heating it with phenol and phosphorus oxychloride at 120°, which melts at 49°, and is hydrolysed by boiling alkali.

Methylxanthone [Me = 3], melting at 176°, is obtained from the

phenyl salt (homosalol) by Seifart's method; whilst dimethylxanthone, $C_6H_3^3Me<^{CO}_{-O-}>C_6H_3^3Me$, is produced by heating the hydroxytoluic acid with acetic anhydride; it melts at 166°. A. R. L.

Diamidosulphobenzide and its Derivatives. By C. Lauth (*Compt. rend.*, **114**, 1023—1024).—Diamidosulphobenzide is easily obtained in the following way. One part of sulphobenzide is dissolved in 3 parts of nitric acid of 48° B., and mixed with 5 parts of sulphuric acid. Heat is developed, and the temperature is maintained for half an hour. The crystalline mass which forms on cooling is washed with water, and the product recrystallised from alcohol until its melting point is 197°. The dinitrosulphobenzide is reduced by heating it with one and a half times its weight of tin, and three times its weight of hydrochloric acid, and the product is crystallised from alcohol or benzene. Diamidosulphobenzide forms rhomboïdal prisms, melting at 165—170°, and soluble in hot water, hot alcohol, or hot benzene, from all of which it crystallises on cooling.

Diamidosulphobenzide is not attacked by zinc and sulphuric acid. It readily yields diazo-derivatives, and these form the usual colouring matters with naphthols, amines, &c.

Tetrazo-colouring matters can also be formed in the usual way, but although these various colouring matters are of great beauty, they have no important advantages over the known dyes, and have very little affinity for cotton. C. H. B.

Dibenzylcarbinamine. By W. A. Noyes (*Amer. Chem. J.*, **14**, 225—230; compare Bamberger, Abstr., 1889, 892).—This base was obtained on reducing dibenzylketoxime with sodium and absolute alcohol. The alcoholic solution was distilled in a current of steam to drive off the alcohol, and the residual alkaline solution was diluted slightly, and allowed to cool, when the base, together with some unchanged oxime, separated as an oily liquid. The oil was freed from the alkaline solution, and converted into the hydrochloride by the addition of dilute hydrochloric acid. The solution was neutralised with soda, and then rendered slightly acid with acetic acid, whereby the unchanged oxime separated almost completely. The clear solution, on the addition of soda, yielded the base in an almost pure condition.

Dibenzylcarbinamine melts at 47°, and boils without decomposition at 330°; it has a strong alkaline reaction, and dissolves readily in alcohol, ether, and light petroleum, but is nearly insoluble in water. The *hydrochloride*, $C_{15}H_{15}\cdot NH_2,HCl$, separates in compact crystals, which group themselves in nodular aggregates, is moderately soluble in water, and melts at 205°. The *platinochloride*, $(C_{15}H_{15}\cdot NH_2)_2,H_2PtCl_6$, forms light-yellow, crystalline scales, which may be recrystallised from water without decomposition. The *nitrite*, $C_{15}H_{15}\cdot NH_2,HNO_2$, is precipitated in long, interwoven, slender needles when sodium nitrite is added to a concentrated solution of the hydrochloride. Its solution is perfectly stable at the ordinary temperature, but when a

concentrated solution is heated to the boiling point, nitrogen is evolved, and dibenzylcarbinol is formed as the chief product of the decomposition.

Dibenzylcarbinamine dibenzylcarbinaminethiocarbamate,

$$C_{15}H_{15}\cdot NH\cdot CSSH, C_{15}H_{15}\cdot NH_2,$$

is formed by the addition of dibenzylcarbinamine to carbon bisulphide. It melts at 141—143°, and simultaneously decomposes with evolution of hydrogen sulphide, and probable formation of the substituted thiocarbamine, $C_{15}H_{15}\cdot NH\cdot CS\cdot NH\cdot C_{15}H_{15}$.

Dibenzylcarbinol, $CH(CH_2Ph)_2\cdot OH$, obtained on heating the concentrated aqueous solution of the nitrite described above, is a viscous liquid, heavier than water, and of a pale-yellow colour, the colour being probably due to impurities. It boils at about 320—325°.

It appears from the above that the nitrite of dibenzylcarbinamine is more stable than the nitrites of most aliphatic amines. It has not, however, the same stability as the nitrites of the alicyclic amines, and the latter form a class distinct in their properties from all other amines at present known. G. T. M.

Formation of Aromatic Nitriles. By H. A. Michaël and J. Jeanprêtre (*Ber.*, **25**, 1615—1619).—Diphenylacetonitrile, $CHPh_2\cdot CN$, is prepared by heating phenylhydroxyacetonitrile (1 part) with benzene (2 parts) and phosphoric anhydride (1 part) on the water-bath for five hours; the product is washed with water, and the residue extracted repeatedly with benzene; the yield is one-third of the nitrile employed.

Toluene and phenylhydroxyacetonitrile yield in a similar manner tolylphenylacetonitrile, $C_6H_4Me\cdot CHPh\cdot CN$; it is desirable to employ stannic chloride instead of phosphoric anhydride as the dehydrating agent; the yield is 30 per cent. of the theoretical. The corresponding acid is obtained by heating the nitrile with concentrated alcoholic potash for six hours in a reflux apparatus.

Phenyltrimethylphenylacetonitrile, $C_6H_2Me_3\cdot CHPh\cdot CN$, is obtained by heating phenylhydroxyacetonitrile (3 parts), mesitylene (2 parts), and stannic chloride (1 part) for six hours on the water-bath; it crystallises from dilute alcohol and light petroleum in pale-yellow prisms, melts at 91°, and boils at 220—230° under a pressure of 40 mm.; the yield is 40 per cent. of the theoretical.

Naphthylphenylacetonitrile, $C_{10}H_7\cdot CHPh\cdot CN$, is prepared in a similar manner to the preceding compound, chloroform being employed as solvent; it crystallises from alcohol in colourless prisms, melts at 97°, and boils at 280° under a pressure of 45 mm.; the yield is 40—50 per cent., but is reduced to 10—12 per cent. by the substitution of phosphoric anhydride for the stannic chloride.

Naphthylphenylacetic acid, $C_{10}H_7\cdot CHPh\cdot COOH$, is obtained by heating the preceding compound with alcoholic potash, and is deposited from alcohol in colourless, prismatic crystals, melting at 141°. The *potassium salt* crystallises from water in colourless, lustrous plates. J. B. T.

Ammonium Bases of Phenylacridine. By A. Bernthsen (*Ber.*, **25**, 1746—1747).—The author has repeated his former experiments, and acknowledges the accuracy of Decker's statements (this vol., p. 881) respecting the product of the interaction of phenylacridine methiodide and sodium hydroxide. He finds that the methylphenylacridineammonium ethoxide which is obtained by crystallising the product from alcohol melts at 111°. A. R. L.

Azo- and Alkyl-compounds of Chrysaniline and the Colouring Matters derived from them. By A. Trillat and de Raczkowski (*Compt. rend.*, **114**, 1024—1026).—Diamidophenylacridine is easily prepared by dissolving commercial phosphine in a large quantity of acidified water, and pouring the liquid slowly, with constant agitation, into a dilute solution of sodium carbonate. The base separates as a yellow powder, and is easily diazotised in the usual way. The tetrazoic compound thus obtained readily combines with amines, phenols, &c. The compound obtained by the action of tetrazochrysaniline (1 mol.) on sodium naphtholdisulphonate (2 mols.) forms a green powder with a metallic lustre. It is insoluble in alcohol, but very soluble in water, forming a red solution. The colouring matters obtained with the phenolsulphonates vary in tint from rose to bright-red. Silk dyes readily, wool in an acid bath dyes badly, and non-mordanted cotton does not dye. Cotton mordanted with tannin acquires only a feeble tint. In solidity, brilliance, and resistance, the colours are inferior to those obtained with chrysaniline.

When chrysaniline is heated under pressure with methyl alcohol and methyl iodide, it yields brilliant crystals of the compound $C_{20}H_{12}Me_3N_3,2HI$, and the ethyl derivative can be obtained in a similar manner. The salts are only slightly soluble, and the solutions dye silk and cotton orange-red, but the colours are inferior to those given by the salts of chrysaniline.

Benzylchrysaniline is obtained by adding benzyl chloride to a warm alcoholic solution of chrysaniline. Sufficient lime to neutralise the hydrochloric acid is then added very gradually, and the product forms a red powder which has not yet been crystallised. It is soluble with difficulty even in dilute acids, and in tinctorial properties is very similar to the methyl and ethyl derivatives. C. H. B.

Desaurin. By W. Wachter (*Ber.*, **25**, 1727—1732).—By employing the following modification of V. Meyer and Oelkers' method of preparing deoxybenzoïn (Abstr., 1888, 703), larger quantities of material can be dealt with without minimising the yield. Benzoïn is heated on the water-bath with alcohol and granulated zinc in a reflux apparatus, a continuous current of hydrogen chloride being passed through meanwhile; 40 grams of deoxybenzoïn, sufficiently pure for direct use, is obtained from 50 grams of benzoïn. In the preparation of desaurin by V. Meyer and Wege's method (this vol., p. 340), the residue after distilling off the carbon bisulphide is well mixed with water, and washed by decantation to remove the alkali, and subsequently digested with alcohol and ether. When extracted with

ether until the latter is no longer coloured, it is sufficiently pure for use.

When desaurin is triturated with concentrated sulphuric acid (100 parts), and fuming nitric acid dropped in until a yellowish-brown solution is formed, and the latter poured into water, a yellow compound is obtained, giving, on analysis, numbers agreeing best with the formula $C_{13}H_9SN_3O_8$; whilst when desaurin (0·2 gram at most) is dissolved in fuming nitric acid (5 parts), a compound is produced resembling the first, but giving analytical values leading to the formula $C_{11}H_8SN_3O_{10}$. Both compounds melt with decomposition at 60°, and dissolve in concentrated sulphuric acid with a yellow colour; metanitrobenzoic acid is in each case simultaneously formed.

Triphenylguanidine (m. p. 127°) is obtained by heating desaurin in a reflux apparatus, for a day with aniline (10 parts); whilst on further heating and allowing the product to remain in the air, deoxybenzoïn, benzanilide, and benzile were also isolated. When desaurin is heated with hydriodic acid, or dry zinc-dust, stilbene is formed; whilst on fusing it with potash benzoic acid is produced.

A. R. L

Phenolphthaleïn Ethyl Ether. By E. Grande (*Chem. Centr.*, 1892, i, 380—381, from *Ann. Chim. Farm.*, **14**, 331—333).—The *ethyl ether of phenolphthaleïn*, $CO<\begin{matrix}C_6H_4\\O\end{matrix}>C<\begin{matrix}C_6H_4\cdot OEt,\\C_6H_4\cdot OH\end{matrix}$, is obtained by bringing phenol and phenetoïlphthaloylic acid together in presence of aluminium chloride. The ether forms a white, crystalline mass melting at 85°, and gives a red-violet coloration with alkalis. The ammonia solution decolorises more readily than that of phenolphthaleïn.

J. W. L.

Hydroxyxanthones. By S. v. Kostanecki and R. Rutishauser (*Ber.*, **25**, 1648—1653).—2-Hydroxyxanthone is obtained, together with diacetylquinol, when salicylic acid and quinol are distilled with acetic anhydride. The crude product is gently heated with concentrated sulphuric acid, and the solution poured into water, when the xanthone separates; it is extracted with warm, dilute sodium hydroxide, and reprecipitated from the solution by acid; it crystallises from aqueous alcohol in yellowish needles, and melts at 231°; the acetyl derivative forms white needles, and melts at 161°.

4-*Hydroxyxanthone* is formed, together with diacetylcatechol, when salicylic acid and catechol are distilled with acetic anhydride. The crude product is extracted with sodium hydroxide and the solution acidified, when the xanthone separates, and is purified by crystallisation from alcohol in the presence of animal charcoal; it forms small, white needles, and melts at 224°; the *sodium* salt crystallises from sodium chloride solution in citron-yellow needles; whilst the *acetyl* derivative crystallises from dilute alcohol in white, microscopic needles, and melts at 137—138°.

The so-called α- and β-hydroxyxanthones, obtained by condensing salicylic acid with resorcinol, contain the hydroxyl group in positions 1 or 3. The β-compound dissolves in concentrated sulphuric acid, forming an almost colourless solution with a bluish fluorescence,

and gives an acetyl derivative which crystallises from dilute alcohol in white, silky needles melting at 157—158°. A. R. L.

Bye-products in the Preparation of Hydroxyxanthones. By S. v. Kostanecki and S. Seidmann (*Ber.*, **25**, 1654—1658).—When the distillate obtained from salicylic acid, resorcinol, and acetic anhydride is boiled with alcohol, the xanthone and the two dihydroxyxanthones dissolve leaving a residue consisting of *dixanthone*, $C_{20}H_{10}O_4$; it crystallises from glacial acetic acid in bunches of needles, resembling xanthone, melts at 256°, and dissolves in concentrated sulphuric acid, forming a solution having a greenish fluorescence. The same dixanthone is obtained from both α- and β-hydroxyxanthone.

When the distillate from salicylic acid and phloroglucinol is boiled with alkali, 1 : 3-isoeuxanthone (Abstr., 1891, 1061) dissolves; the residue is collected and treated with hydrochloric acid, and consists of two isomeric hydroxydixanthones,

$$C_6H_4<\begin{matrix}O\\CO\end{matrix}>C_6H(OH)<\begin{matrix}O\\CO\end{matrix}>C_6H_4,$$

which may be separated as follows:—The substance is boiled with acetic anhydride and sodium acetate, and the product dissolved in boiling glacial acetic acid, when *β-hydroxydixanthone* separates on cooling, whilst *acetyl α-hydroxydixanthone* is obtained on adding water to the filtrate; the latter crystallises from alcohol in white needles, melts at 213°, and yields the *α-hydroxydixanthone* (m. p. 258°; this vol., p. 504) on boiling it with alkali, and treating the resulting sodium salt with acid; β-hydroxydixanthone crystallises from glacial acetic acid in yellow tables, melts at 326°, and remains unaltered after 24 hours treatment by the usual acetylation method.

A. R. L.

1 : 4-Amidonaphthyl Ethyl Ether and some Derivatives. By P. Heermann (*J. pr. Chem.* [2], **45**, 545—553; compare Abstr., 1891, 1379).—1 : 4-Amidonaphthyl ethyl ether (this vol., p. 862) melts at 96°, and dissolves in the usual solvents, except water and strong hydrochloric acid; it sublimes and distils partially, and is diazotised with difficulty. The hydrochloride decomposes about 275°, and the *sulphate* melts about 240°. The *acetyl* derivative, $OEt{\cdot}C_{10}H_6{\cdot}NHAc$, is easily prepared by heating the ether with anhydrous sodium acetate, glacial acetic acid, and a couple of drops of acetic anhydride; it crystallises in silvery laminæ, melts at 192°, and dissolves easily in alcohol and glacial acetic acid, but sparingly in water; although, like phenacetine, undoubtedly antipyretic, it is not available on account of its poisonous effects. The *diacetyl* derivative, $OEt{\cdot}C_{10}H_6{\cdot}NAc_2$, obtained by the further action of acetic anhydride, crystallises in laminæ or prisms, melts at 138°, and is sparingly soluble in organic solvents and hardly at all soluble in water; ammonia or sodium hydroxide converts it into the acetyl derivative. The *benzoyl* derivative, prepared as usual from the hydrochloride, benzoic chloride, and sodium hydroxide, crystallises from alcohol in white needles, melts at 214—215°, and is very sparingly soluble in hot alcohol.

Attempts to nitrate the foregoing derivatives always resulted in the formation of α-naphthaquinone as a main product. A small quantity of *nitracetamidonaphthyl ethyl ether* [OEt : NO_2 : NHAc = 1 : 3 : 4] was, however, obtained; this crystallises in slender, yellow needles, melts at 221°, and is sparingly soluble in alcohol; its orientation was settled (1) by converting it into phthalic acid by nitric acid (sp. gr. 1·135) in a sealed tube at 180—200°, and (2) by reducing it with iron filings and hydrochloric acid, whereby *ethenyldiamidonaphthyl ethyl ether*, $OEt{\cdot}C_{10}H_5{<}^{N}_{NH}{>}CMe$, is obtained; the first experiment settles the ring in which the nitro-group is, whilst the second is evidence that the nitro-group is in the ortho-position to the acetylamido-group (compare this vol., pp. 837, 631 and 632). The last-mentioned compound crystallises in slender laminæ, melts at 179°, dissolves in alcohol and ether, and sparingly in hot water; its *bromine* derivative was prepared by brominating it in glacial acetic acid.

A. G. B.

Hydroxyquinones. By M. Kowalski (*Ber.*, **25**, 1658—1661).—Groves has already observed (this Journal, 1873, 210) that α-naphthaquinone dissolves in alkalis with the formation of a reddish-brown solution from which acids precipitate a red substance. When dilute aqueous alkali is added to finely-pulverised α-naphthaquinone, and the mixture shaken and exposed to the air for a time, the quinone dissolves, and, on boiling with barium carbonate mixed into a paste with water the precipitate obtained by adding acid to the solution and filtering while hot, a crystalline barium salt separates from the filtrate on cooling; this is purified, dissolved in water, and hydrochloric acid added to the solution, when hydroxy-α-naphthaquinone, amounting to 20 per cent. of the α-naphthaquinone employed, separates. By treating thymoquinone in a similar manner with alkali, and distilling the crude, acidified product in a current of steam, a mixture of hydroxy- and dihydroxy-thymoquinone passes over; the mixture is dissolved in alcohol and lead acetate added, when the lead salt of the dihydroxy-derivative separates, whilst the monhydroxy-compound remains in solution. Favourable results were not obtained with benzoquinone, and Woskresensky's melanic acid (*J. pr. Chem.*, **34**, 251) seems not to have the properties of a hydroxyquinone.

Whereas Kostanecki has shown (Abstr., 1889, 887) that hydroxy-α-naphthaquinone yields a quinoneoxime when treated with hydroxylamine, the author finds that when hydroxylamine hydrochloride is added to an alkaline solution of hydroxythymoquinone, and the solution is acidified with acetic acid, a flocculent precipitate separates; it crystallises from dilute alcohol in brown leaflets, melts at 190°, and is a *hydroxyamidothymoquinone*. It gives dihydroxythymoquinone on heating it with hydrochloric acid at 180°. Hydroxythymoquinone, therefore, behaves towards hydroxylamine in an analogous manner to pipitzahoic acid (see Anschütz and Leather, Trans., 1886, 721).

A. R. L.

Xanthones and Hydroxyxanthones of the Naphthalene and Quinoline Series. By S. v. Kostanecki (*Ber.*, **25**, 1640—1647).

—Dinaphthoxanthone, $C_{10}H_6<^{CO}_{O-}>HC_{106}$, melting at 240°, and identical with the compound described by Bender (Abstr., 1881, 48), is obtained by distilling 1 : 2-naphtholcarboxylic acid with acetic anhydride; it dissolves in concentrated sulphuric acid, forming a faintly-yellow solution, having a greenish fluorescence. An isomeride melting at 216°, also described by Bender (Abstr., 1887, 38), is obtained from 2 : 1-naphtholcarboxylic acid (m. p. 157°); its solution in concentrated sulphuric acid is yellow, with a strong green fluorescence. 3 : 4-Naphtholcarboxylic acid (m. p. 216°), prepared from β-naphthol by Schmitt's method, yields a *xanthone* crystallising in yellow needles and melting at 241°, which dissolves in concentrated sulphuric acid to a brownish-yellow solution devoid of fluorescence.

Phenonaphthoxanthone, $C_6H_4<^{O-}_{CO}>C_{10}H_6$, is obtained, together with xanthone and the above-mentioned dinaphthoxanthone, when a mixture of salicylic acid and 1 : 2-naphthocarboxylic acid is distilled with acetic anhydride; it is separated from the accompanying products by means of its more sparing solubility in alcohol, and melts at 155°; it is identical with Graebe and Früh's α-naphthophenone oxide (Abstr., 1887, 152), and its solution in concentrated sulphuric acid has a very strong green fluorescence. The isomeric compound, identical with Graebe and Früh's β-naphthophenone oxide (*loc. cit.*), is obtained in the same manner from both the above-mentioned β-naphtholcarboxylic acids. The two phenonaphthoxanthones are, however, produced in better yield by distilling α- or β-naphthol and salicylic acid with acetic anhydride.

1-Hydroxyquinoline does not give a xanthone on distillation with salicylic acid and acetic anhydride, but 4-hydroxyquinoline gives the *phenoquinolinoxanthone*, $C_6H_4<^{O-}_{CO}>C_9NH_7$ [O : CO = 3 : 4 or 2 : 3]; it crystallises from alcohol in white needles, melts at 188°, and its solution in concentrated sulphuric acid has a faint green fluorescence; the *hydrochloride* forms white needles. Three isomeric hydroxyphenonaphthoxanthones are obtained from the three naphthocarboxylic acids mentioned above; better results are, however, obtained as follows:—Hydroxyphenonaphthoxanthone [O : CO : OH = 1 : 2 : 4′] is produced from salicylic acid and 1 : 4′-dihydroxynaphthalene; it crystallises from alcohol in yellow needles, melts at 270°, and its solution in concentrated sulphuric acid exhibits a greenish fluorescence; its sodium salt is orange-yellow, and sparingly soluble in water, and its *acetyl* derivative melts at 216°. *3′-Hydroxy-β-naphthoxanthone*, prepared from 2 : 2′-dihydroxynaphthalene, melts at 290°, forms a *sodium* salt crystallising in golden-yellow leaflets, and an *acetyl* derivative melting at 206°. A. R. L.

Xanthones and Hydroxyxanthones of the Naphthalene Series. By P. Bener (*Chem. Centr.*, 1892, i, 388; from *Schweiz. Wochenschr. Pharm.*, **30**, 29).—Of the naphtholcarboxylic acids, three are obtained commercially, one being prepared from α-naphthol, and two from β-naphthol. All three acids react with acetic anhydride, forming

naphthoxanthones, which differ from one another; also with salicylic acid, three different phenonaphthoxanthones are formed. By distilling the three carboxylic acids with dihydroxyphenols, hydroxyxanthones are formed. Those obtained from resorcinol form, with soda, intensely yellow-coloured, insoluble sodium salts. With salicylic acid, the dihydroxynaphthalenes form the corresponding dihydroxyxanthones, but the hydroxyl group is present in the naphthalene ring. The sodium salt of the hydroxyphenonaphthoxanthone, obtained from β-β_3-dihydroxynaphthalene, is sparingly soluble in water, and crystallises in golden-yellow needles. Finally, the three naphtholcarboxylic acids condense, with the dihydroxynaphthalenes, forming hydroxynaphthoxanthones. J. W. L.

Benzeneazo-α-naphthylglycocine. By A. Donner (*Ber.*, **25**, 1605—1610; compare Abstr., 1891, 191).—*Paranitrobenzeneazo-α-naphthylglycocine* is prepared by the action of a α-naphthylglycocine in hydrochloric acid solution on paranitrodiazobenzene chloride, and is almost insoluble in water, benzene, or carbon bisulphide; it melts at 125° with decomposition, has a greenish lustre, and dissolves in alcohol, acetone, or chloroform with a red colour; with sulphuric acid, a blue coloration is obtained which changes to red on dilution; in alcoholic solution, silk is dyed violet. The *hydrochloride*,

$$C_{18}H_{14}N_4O_4,HCl,$$

is a lustrous, green powder, melting at 178°, it is dichroic, and appears to be bluish-red in transmitted light.

The *potassium salt*, $3C_{18}H_{13}N_4O_4K,C_{18}H_{14}N_4O_4$, forms a dark-green powder, which melts at 224—226°, and imparts a brownish-red colour to silk.

Orthonitrobenzeneazo-α-naphthylglycocine resembles the para-compound and is obtained in a similar manner; it melts at 94—96° with decomposition, and exhibits dichroism. The *hydrochloride* melts at 147°. The *potassium salt*, $C_{18}H_{13}N_4O_4K,C_{18}H_{14}N_4O_4$, is brown and dissolves sparingly in water with a yellowish-red colour, which changes to red on the addition of acetic acid, and by adding hydrochloric acid to this solution the colour once more changes to violet.

Metanitrobenzeneazo-α-naphthylglycocine, prepared from metanitrodiazobenzene chloride and α-naphthylglycocine, is deposited in small, blue needles, which melt at 139° with evolution of gas; it is insoluble in water and in most other media, but dissolves in concentrated hydrochloric acid with a yellow colour, and in sulphuric acid with a deep-blue colour.

The *hydrochloride* is reddish-brown, and melts at 177°. The *potassium salt*, $C_{18}H_{13}N_4O_4K$, readily dissolves in water, and the solution becomes gelatinous on cooling; it crystallises in small, yellowish-brown needles which melt at 213—214°. J. B. T.

Terpenes and their Derivatives. By J. W. Brühl (*Ber.*, **25**, 1788—1796, 1796—1813; compare this vol., pp. 200, 547, 624).—It has been recently suggested by Friedel (this vol., p. 500) that camphoric acid is a ketohydroxymonocarboxylic acid of the constitu-

tion $CHPr<^{CH_2\cdot CO}_{CH_2\cdot CH_2}>C(OH)\cdot COOH$; if this view is correct, it is to be presumed that camphoric acid would readily undergo oxidation, which is by no means the case. It would also be expected that the acid would be converted into a dihydroxy-compound on reduction and have numerous other properties which are not possessed by camphoric acid.

The author has investigated the behaviour of camphoric acid with sodium in boiling alcoholic and in boiling cumene solution; he finds that the acid is not reduced, although camphor, which, according to Friedel, has a constitution analogous to that of camphoric acid, is readily reduced under similar conditions. Attempts to reduce camphoric anhydride by treating it with sodium and borneol were also unsuccessful; under these conditions the anhydride is for the most part carbonised.

It was also proved that both camphoric acid and methyl camphorate do not interact with hydroxylamine or with phenylhydrazine under the conditions which are usually most favourable to the production of oximes and hydrazones.

When a neutral solution of sodium camphorate is treated with excess of sodium hydrogen sulphite, camphoric acid is liberated; camphoric acid does not reduce Fehling's solution even on boiling.

Ethyl camphorate is not acted on by phosphorus pentachloride at the ordinary temperature, nor by sodium and carbonic anhydride under the conditions previously described (this vol., p. 201) in the case of camphor.

When camphoric acid (2 mols.) is warmed with sodium carbonate (1 mol.), approximately half of the acid remains uncombined; both the ortho- and the allo-monalkyl salts of camphoric acid (see later) dissolve in sodium carbonate with liberation of carbonic anhydride, showing that both the hydroxy-groups in camphoric acid have an acid character and are not alcoholic or phenolic in function.

Picric acid does not yield an ethyl derivative on treatment with alcohol and hydrogen chloride; camphoric acid, under the same conditions, gives diethyl camphorate.

All the above facts go to show that Friedel's formula for camphoric acid is untenable; in the author's opinion the tetramethylene formula is, at present, the most probable and the one most securely based on facts.

In the following, the term "ortho-" is given to that alkyl group which is first introduced into the camphoric acid molecule; the second alkyl group is distinguished by the term "allo-."

Orthethyl allomethyl camphorate, $C_{10}H_{14}O_4EtMe$, is obtained when orthethyl hydrogen camphorate, prepared as previously described, is heated with methyl iodide and sodium methoxide at 100° for five hours. It is a yellowish, moderately mobile liquid, boils at 169·5° under a pressure of 33 mm., and at 276·5—275° under a pressure of 746 mm. Its sp. gr. is 1·0548, 20°/4°; 1·0569, 17·7°/4°. $\mathfrak{M}_\alpha = 62{\cdot}49$, $\mathfrak{M}_{Na} = 62{\cdot}76$, $\mathfrak{M}_\gamma - \mathfrak{M}_\alpha = 1{\cdot}47$ (compare this vol., p. 347), results which agree well with the calculated values for $C_{13}H_{22}O_2<O''_2$. Its specific rotatory power is $[\alpha]_D = 38{\cdot}43°$.

Orthomethyl alloethyl camphorate, prepared from orthomethyl hydrogen camphorate in like manner, is a yellowish liquid boiling at 175° under a pressure of 38 mm., and at 278° under a pressure of 747 mm.; its sp. gr. is 1·0467, 20°/4°; 1·0492, 17·1°/4°. $\mathfrak{M}_\alpha = 62{\cdot}77$, $\mathfrak{M}_{Na} = 63{\cdot}04$, $\mathfrak{M}_\gamma - \mathfrak{M}_\alpha = 1{\cdot}47$; $[\alpha]_D = 45{\cdot}49°$. It will be seen that practically the only difference between this ethereal salt and the compound just described is that the latter is more strongly dextrorotatory.

Alloethyl hydrogen camphorate, $C_{12}H_{20}O_4$, is obtained when orthomethyl alloethyl camphorate is mixed with a 16 per cent. solution of alcoholic potash (2 mols.), the mixture kept for 20 hours at the ordinary temperature, and then boiled for 15 minutes. It separates from light petroleum in transparent, rhombic, hemimorphic plates, $a : b : c = 1{\cdot}6184 : 1 : 3{\cdot}1877$, and melts at 57°. It is much more stable towards potash than the orthethyl hydrogen salt.

Diethyl camphorate, prepared by treating camphoric acid with alcohol and hydrogen chloride, has a specific rotatory power $[\alpha]_D = 36{\cdot}30°$, and is identical with the compound obtained by Friedel (*loc. cit.*) by the action of ethyl iodide on silver camphorate; on treatment with alcoholic potash under the conditions described above, it is converted into alloethyl hydrogen camphorate (m. p. 57°).

Allomethyl hydrogen camphorate, $C_{11}H_{18}O_4$, is formed when orthethyl allomethyl camphorate is boiled for 30 minutes with 16 per cent. alcoholic potash; it crystallises from hot water in long, colourless, spear-shaped forms, melts at 86—87°, and is readily soluble in alcohol, ether, light petroleum, &c.

Orthomethyl hydrogen camphorate, $C_{11}H_{18}O_4$, is obtained, together with dimethyl camphorate, when camphoric acid is treated with methyl alcohol and hydrogen chloride in the manner previously described (*Ber.*, **24**, 3409). It separates from hot water in well-defined, rhombic, hemihedric plates, $a : b : c = 0{\cdot}6316 : 1 : 1{\cdot}2870$, melts at 77—78°, and boils at 223° under a pressure of 21 mm.; it is readily soluble in ether, alcohol, light petroleum, &c., and is much less stable towards potash than the corresponding allomethyl salt.

Dimethyl camphorate, $C_{10}H_{14}O_4Me_2$, is a thick, almost colourless liquid boiling at 149·5° under a pressure of 11 mm., and at 264° under a pressure of 738 mm.; its sp. gr. is 1·0747, 20°/4°; 1·0774, 16·9°/4°. $\mathfrak{M}_\alpha = 58{\cdot}07$, $\mathfrak{M}_{Na} = 58{\cdot}32$, $\mathfrak{M}_\gamma - \mathfrak{M}_\alpha = 1{\cdot}37$, values which agree well with those calculated for $C_{12}H_{20}O_2{<}O''_2$; its specific rotatory power is $[\alpha]_D = 48{\cdot}16°$. When warmed for half an hour with dilute alcoholic potash, it is converted into allomethyl hydrogen camphorate (m. p. 86—87°).

Although the existence of the isomerides described above can be easily accounted for on the basis of Friedel's formula for camphoric acid (see above), there are certain facts which could not very well be explained in the same way, amongst others the formation of the dialkyl salts on treating the acid with hydrogen chloride and an alcohol, and the decomposition of both the isomeric monalkyl salts by dilute potash. Assuming that camphoric acid is methylpropyltetramethylenedicarboxylic acid, the existence of two series of alkyl hydrogen salts is also easily accounted for, because the two carboxy-

groups must be unequally strong. The fact that the alkyl group which is first introduced into the camphoric acid molecule is also the first to be expelled on hydrolysis, viewed in the light of the present dissociation hypothesis of electrolytes, is only what would be expected on *a priori* grounds; the orthoalkyl derivatives which are first formed are the less stable isomerides, and, therefore, when an orthoallo-salt is submitted to hydrolysis, the orthoalkyl group is the first to be eliminated.

The author has repeated Friedel's experiments on the titration of camphoric acid, employing either litmus, corallin, or phenolphthaleïn as indicator; the results show clearly that camphoric acid is a true dicarboxylic acid. In the case of litmus, the change of colour is not quite sharp, phenolphthaleïn being the best indicator; methyl-orange cannot be employed. F. S. K.

Constitution of Camphoric Acid. By F. Stohmann and C. Kleber (*J. pr. Chem.* [2], **45**, 475—499).—See this vol., p. 1040.

Eupatorin: The Active Principle of Eupatorium perfoliatum. By C. H. Shamel (*Amer. Chem. J.*, **14**, 224—225).—The dried *Eupatorium perfoliatum*, gathered at blooming time, was extracted with hot alcohol for several hours. The alcohol was distilled off, and the residue was treated with dilute hydrochloric acid, whereby a black, gummy mass separated, which was removed by filtration. The filtrate was neutralised with sodium carbonate and extracted with ether. On evaporation of the ethereal solution, the active principle was deposited either as a yellow, amorphous mass or as a yellow, microcrystalline powder. It contains no nitrogen, does not melt, but decomposes at 250°, is insoluble in water and in concentrated sulphuric and hydrochloric acids, but dissolves in dilute nitric acid forming a light-brown solution, which, when allowed to evaporate spontaneously, furnishes beautiful prisms and six-sided plates. These crystals of the *nitrate* are readily soluble in water, and the solution has a strong toxicological effect. They melt at 102—103°, and, when deprived of their water of crystallisation, give numbers, on analysis, which indicate that their formula is

$$C_{20}H_{25}O_{36},HNO_3.$$ G. T. M.

Action of Pyridine Bases on Sulphites. By G. Denigès (*Compt. rend.*, **114**, 1018—1020).—Pyridine bases do not form conjugated compounds with any metallic hydrogen sulphites, or compounds with any normal sulphites except those of zinc and cadmium.

30 grams of zinc sulphate is dissolved in 700 c.c. of water and mixed with 25 c.c. of pyridine and 60 c.c. of a solution of sodium hydrogen sulphite of sp. gr. 1·38. There is immediate formation of a white, crystalline precipitate, very slightly soluble in water. The product has the composition $ZnSO_3,C_5NH_5$, and forms quadratic needles that are optically negative. Other pyridic bases behave differently, and the precipitate consists simply of zinc sulphite, $2ZnSO_3 + 5H_2O$. Manganese sulphate also gives a precipitate of manganese sulphite alone. Possibly in these cases unstable pyridine

compounds are formed which dissociate with precipitation of the metallic sulphites.

When a 10 per cent. solution of cadmium nitrate is mixed with at least one-fifth of its volume of pyridine and one-fifth of its volume of sodium hydrogen sulphite solution of sp. gr. 1·38, there is no immediate precipitate; but on vigorous agitation and rubbing of the sides of the vessel with a glass rod, a mass of white, highly refractive, optically negative, quadratic needles gradually separates. This product has the composition $CdSO_3,C_5NH_5$, and dissociates somewhat easily into its proximate constituents. The compound can be obtained from warm solutions if the proportion of pyridine is doubled, but is less pure. If the proportion of pyridine is not increased, anhydrous cadmium sulphite alone separates. Even in the cold, if the proportion of pyridine is reduced to one-half, there is immediate formation of a very bulky precipitate of the composition $2CdSO_3 + 3H_2O$.

Zinc pyridine sulphite is much more stable than the cadmium compound. C. H. B.

Oxidation of Reduced Pyridine and Quinoline Bases. By J. Tafel (*Ber.*, **25**, 1619—1623).—Piperidine may be readily oxidised to pyridine by dissolving the pure base (2·5 grams) in 10 per cent. acetic acid (25 c.c.) and heating the solution with silver acetate (30 grams) in a sealed tube for four hours at 180°; the contents of the tube are treated with water, filtered, and the filtrate distilled over potash, the distillate, consisting of a mixture of pyridine and piperidine, is treated with sulphuric acid in slight excess and again distilled, the operation being repeated if needful; the piperidine remains behind as sulphate; the yield is 35 per cent. of pyridine and 25 per cent. of unaltered piperidine.

Conyrine may in a similar manner be obtained from coniine by heating it with the calculated quantity of silver acetate; the yield is 32·5 per cent., whilst 43—44 per cent. of unaltered coniine is recovered.

Tetrahydroquinoline (5 grams) is mixed with 5 parts of mercuric acetate, dissolved in an equal weight of water, and heated in a sealed tube for six hours at 150°; the product is distilled in a current of steam, and the oily distillate treated with hydrochloric acid and sodium nitrite. After remaining for some time, it is extracted with ether, the aqueous solution is rendered alkaline, and the quinoline separated by treatment with ether; the yield is 75 per cent. of the theoretical.

By the action of silver acetate on nicotine, a basic substance is obtained which is sparingly soluble in water, boils at 275°, and appears to be identical with a compound prepared by Cahours and Étard.

Quinoline is also formed by heating tetrahydroquinoline with mercuric oxide, silver nitrate, or silver oxide, but considerable quantities of resinous bye-products are produced. J. B. T.

1 : 4-Ethoxyacetamidoquinoline (Analgen). By G. N. Vis (*J. pr. Chem.* [2], **45**, 530—545).—The author found that the best method for preparing 1-ethoxyquinoline is that of O. Fischer and

Renouf (Abstr., 1883, 1146); he has prepared the *argentonitrate*, the *platinochloride*, the *ethiodide* (m. p. 168—169°), and the *ethochloride* (m. p. 125—127°), as also the *platinochloride* of the last named compound.

Dinitro-1-*ethoxyquinoline* is precipitated as microscopic, yellow needles when a mixture of 1-ethoxyquinoline (1 vol.) with nitric acid of sp. gr. 1·52 (4 vols.) is warmed on the water-bath and then poured into water (12 vols.); its melting point varies, being generally 275°. Its *platinochloride* (with 4 mols. H_2O) was prepared.

4 : 1-*Nitroethoxyquinoline* is obtained by diluting the filtrate from the dinitro-derivative with much water (3 litres for every 100 grams of original ethoxyquinoline), washing the precipitate, which separates after a time, with cold water, dissolving it in hot water, and adding ammonia, whereby the nitro-compound is thrown down in microscopic, yellow needles. It melts at 128°, is insoluble in water, but dissolves easily in hot alcohol and in acids, with which it forms salts which are stable in water. The *nitrate* crystallises in microscopic needles and in well formed prisms which melt at 100°; the *hydrochloride* forms white needles, and the *platinochloride* microscopic needles, which melt at 248° with decomposition; the *ethiodide* and the *methiodide* (m. p. 150°) were prepared.

1 : 4-*Hydroxynitroquinoline* is prepared by heating the nitroethoxyquinoline with concentrated hydrochloric acid at 180—190°. It crystallises in aggregates of needles, melts at 178°, and sublimes; hot alcohol dissolves it easily, water with difficulty. It is both basic and acid; the *hydrochloride* forms yellow needles which darken at 235°, and melt at 258°; the *ammonium* salt crystallises in brown needles and dissociates partially when heated, melting at 178°; the *lead*, *copper*, and *silver* salts, and the *platinochloride*, were prepared. The orientation of this hydroxynitroquinoline is settled (1) by the fact that it is the product of the oxidation of Lippmann's 4 : 1-nitrosohydroxyquinoline (Abstr., 1890, 265) by alkaline potassium ferricyanide, and (2) by its yielding 1 : 4-chloronitroquinoline (m. p. 145°) when heated with excess of phosphoric chloride.

1 : 4-*Ethoxyamidoquinoline*, prepared from the nitro-compound by the usual method, crystallises from hot water in beautiful, yellow laminæ (with 1 mol. H_2O) which melt at 70°; when anhydrous, it melts at 114°, and dissolves sparingly in hot water, ether, and benzene, not at all in light petroleum, but freely in alcohol and acids, forming with the latter salts which give intensely coloured solutions. The *monohydrochloride* forms rhombic laminæ and melts at 235°; the *platinochloride* (with $3\frac{1}{2}$ mols. H_2O) melts with decomposition at 255° the *dihydrochloride* was also prepared.

1 : 4-*Ethoxyacetamidoquinoline* is prepared from the amido-compound by heating it with glacial acetic acid and acetic anhydride for some minutes; it crystallises in white needles, melts at 155°, and dissolves easily in alcohol, and to the extent of about 0·7 per cent. in water at the ordinary temperature; in acids, it dissolves with the formation of salts. The *platinochloride* (with $2\frac{1}{2}$ mols. H_2O) begins to decompose at 215°, and is fully decomposed at 225°. Under the name of analgen, this compound is exhibited as an antineuraigic.

The author's experiments on dogs showed that 3 grams daily for several weeks produced no abnormal pathological conditions in the urine; a fatal subcutaneous dose for guinea pigs is $2\frac{1}{2}$—3 grams per kilo. of body weight; in man the molecule is either completely decomposed or the acetyl group only is eliminated, in which case 1 : 4-ethoxyamidoquinoline is to be recognised in the urine by the intense coloration imparted to it by hot acids. A. G. B.

Action of Sodium and Carbonic Anhydride on Antipyrine. By J. W. Brühl (*Ber.*, **25**, 1869—1875; compare this vol., p. 730).—Knorr and Taufkirch have shown (this vol., p. 708) that the substance described by the author as antipyrine alcohol is in reality β-methylamidocrotonanilide, NHMe·CMe:CH·CO·NHPh, and the author, on further investigation, has come to the same conclusion. To obtain the greatest yield of the additive sodium compound, 2 atoms of sodium and 2 mols. of carbonic anhydride are necessary, and it therefore appears probable that in the reaction the pyrazole ring is split between the two nitrogen atoms, the group COONa then combining with each of these atoms; by the action of water, the latter are replaced by hydrogen with formation of methylamidocrotonanilide.

The anilide is gradually decomposed by boiling water or alcohol, and more quickly by dilute acids with formation of acetoacetanilide; the sodium additive compound undergoes this reaction much more readily, the original product being converted by sulphuric acid at 0° into methylamine sulphate and acetoacetanilide.

β-Methylcrotonanilide is readily acted on by phenyl isocyanate and by benzoic chloride with formation of the *phenylcarbamido*-derivative, NHPh·CO·NMe·CMe:CH·CO·NHPh, and the *benzoyl* derivative,

NBzMe·CMe:CH·CO·NHPh,

respectively; the former crystallises in colourless needles melting at 173°, and the latter in small, white needles melting at 175°.

Attempts were made to convert the sodium additive derivative into an ethyl compound, but without success. It was found, further, that methylphenylpyrazole undergoes no change when treated with sodium and carbonic anhydride, which is in favour of Knorr's view that the constitution of the ring in this compound and in antipyrine is not identical. H. G. C.

Condensation of Orthamidobenzaldehyde. By J. Eliasberg and P. Friedländer (*Ber.*, **25**, 1752—1760).—*Orthamidobenzaldehydephenylhydrazone*, $NH_2·C_6H_4·CH:N_2HPh$, crystallises from alcohol in yellowish needles, and from benzene in small plates, melts at 222°, and turns brown on exposure to the air.

When sodium nitrite is carefully added to a solution of orthamidobenzaldehyde in well-cooled concentrated hydrochloric acid, *orthodiazobenzaldehyde* is formed; if the reddish-yellow solution is now treated with sodium hydrogen sulphite, the colour changes to light-yellow, and a crystalline compound, which melts at 146·5° and is probably identical with Fischer and Kuzel's indazole, is produced in small quantities.

A compound melting at 67·5°, which is very probably $\alpha\beta$-dimethylquinoline, is obtained when a few drops of dilute soda are added to a mixture of ethyl methyl ketone and a dilute aqueous solution of orthamidobenzaldehyde; it crystallises from ether in prisms, is volatile with steam, and dissolves freely in mineral acids and in the ordinary organic solvents. The *platinochloride*, $(C_{11}H_{11}N)_2,H_2PtCl_6$, crystallises in light-yellow needles.

Ethylmethylquinoline, prepared from diethyl ketone in like manner, crystallises from light petroleum in prisms, melts at 57°, is volatile with steam, and is only sparingly soluble in water; the *platinochloride*, $(C_{12}H_{13}N)_2,H_2PtCl_6$, separates from water in crystals.

Naphthylquinoline, $C_9NH_6{\cdot}C_{10}H_7$, can be obtained by heating a mixture of orthamidobenzaldehyde and naphthyl methyl ketone with alcoholic soda; the yield is quantitative. It separates from alcohol in colourless crystals, melts at 161°, and is only sparingly soluble in alcohol, and insoluble in water. The sparingly soluble *sulphate*, the *hydrochloride*, and the *chromate* crystallise in slender needles. The *platinochloride* crystallises from alcohol in microscopic, yellow needles, and is very sparingly soluble in water.

α-Methyl-β-acetylquinoline, $C_{12}NH_{11}O$, is formed by the condensation of orthamidobenzaldehyde and acetylacetone in aqueous solution in presence of soda at the ordinary temperature; it crystallises from light petroleum in long, thick needles, melts at 74°, and boils at 306°; it separates from dilute alcohol and from wet ether in crystals melting at 57·5°, which retain some of the solvent. The *hydrochloride* and the *sulphate* are readily soluble in water and alcohol, but the *chromate* is only sparingly soluble, and crystallises in long, yellow needles; the *platinochloride* has the composition $(C_{12}NH_{11}O)_2,H_2PtCl_6$. The *oxime*, $C_{12}NH_{11}{:}NOH$, crystallises from benzene in thick prisms, melts at 143°, and is soluble in soda. The *hydrazone*, $C_{12}NH_{11}{:}N_2HPh$, crystallises from benzene in almost colourless needles, melts at 130°, and quickly decomposes on exposure to the air; its *hydrochloride* forms small, red needles, and is only sparingly soluble in water.

A compound of the composition $C_{20}H_{16}N_2$, probably a dimethyldiquinoyline, is gradually deposited in crystals when a dilute aqueous solution of orthamidobenzaldehyde is treated with a slight excess of acetonylacetone and two drops of soda; it crystallises from dilute alcohol in lustrous stellate groups of needles which contain 2 mols. H_2O and melt at 104—105°; it loses its water at 105—110°, the anhydrous substance melting at 144°. It dissolves freely in hydrochloric acid and in sulphuric acid, but its chromate is only sparingly soluble, and forms forked crystals. The *platinochloride* has the composition $C_{20}H_{16}N_2,H_2PtCl_6$.

When orthamidobenzaldehyde is warmed with phloroglucinol and very dilute soda and the solution then acidified with acetic acid, a voluminous, red substance is precipitated; this product has both basic and acid properties, and is very sparingly soluble in almost all ordinary solvents. The *hydrochloride* crystallises in slender, yellow needles and is decomposed by water, in which it is only moderately easily soluble. The *platinochloride*, $(C_{13}H_9NO_2)_2,H_2PtCl_6$, crystallises from hot dilute hydrochloric acid in red needles containing 2 mols.

H_2O, which are expelled at 130—135°. The *dibenzoyl* derivative, $C_{13}H_7NO_2Bz_2$, prepared by shaking the condensation product with soda and benzoic chloride, crystallises from acetone in almost colourless needles, melts at 163°, and is soluble in acids and in the ordinary organic solvents, but insoluble in water and alkalis, and almost insoluble in light petroleum. The original condensation product is probably a dihydroxyacridine. F. S. K.

Azonium Compounds. By F. Kehrmann and J. Messinger (*Ber.*, **25**, 1627—1636; compare Abstr., 1891, 1109).—By the action of diacetyl on phenylorthophenylenediamine in alcoholic solution, a basic compound is obtained which has the formula $C_{16}H_{14}N_2$, crystallises in light yellow plates, and melts at 180—190°. The substance dissolves in sulphuric acid with a yellow colour, which disappears on dilution; it is very unstable when moist, being readily converted into a dark-red, insoluble powder, which is also formed by boiling the yellow compound with alcohol or treating it with ammonia.

On treatment of orthophenylenediamine hydrochloride with pyruvic acid in aqueous solution, *ketomethylphenyldihydrophenoquinoxaline*, $C_6H_4<^{N:CMe}_{NPh-}>CO$, is formed; it crystallises from alcohol in short, thick plates, melts at 195°, and is insoluble in water, dilute acids, ammonia, or dilute alkalis; the compound dissolves sparingly in ether, glacial acetic acid, and benzene; with sulphuric acid or concentrated hydrochloric acid, it gives a greenish-yellow coloration.

Ketodimethyldihydroquinoxaline, $C_6H_4<^{N:CMe}_{NMe-}>CO$, is prepared in a similar manner to the preceding compound, and is deposited from water at 50° in colourless, fibrous masses, which contain 2 mols. H_2O and melt at 63—64°; on heating at 100°, the anhydrous base is formed; this boils at 308°, crystallises on cooling, and melts at 87°.

Ketomethylethyldihydroquinoxaline, $C_6H_4<^{N:CMe}_{NEt-}>CO$, is obtained in a similar manner to the preceding compound, which it closely resembles, being, however, somewhat more sparingly soluble; it crystallises from water with 2 mols. H_2O in almost colourless, transparent prisms melting at 77°; the anhydrous base melts at 96—97° and boils at 303°.

Ketomethylbenzyldihydroquinoxaline, $C_6H_4<^{N:CMe}_{NBz-}>CO$, crystallises from dilute alcohol in small, slender, colourless, concentric needles, melts at 99—100°, and boils above 350° with partial decomposition; it is insoluble in water, but readily dissolves in ether or benzene.

In the formation of the preceding compounds, the pyruvic acid reacts with alkyl orthodiamines as a ketonic alcohol, whilst with simple orthodiamines it behaves as an orthodiketone.

By the action of benzile on methyl orthophenylenediamine hydrochloride in alcoholic solution, *diphenylmethylethophenazonium hydroxide*, $C_6H_4<^{N=CPh}_{NMe(OH)}>CPh$, is formed, and is purified by means

of the nitrate; it is amorphous, and decomposes at 70°; the base is soluble in benzene with a yellow colour and a bluish-green fluorescence, and in alcohol with a yellowish-green fluorescence; with sulphuric acid, an orange-red coloration is produced, which changes to yellow on the addition of water. The *nitrate* crystallises with 3 mols. H_2O in large, yellow plates, which readily dissolve in water and are precipitated by the addition of nitric acid.

Diamidodiphenylamine, $C_6H_3(NH_2)_2{\cdot}NHPh$ [= 2 : 4 : 1], is prepared by the reduction of the corresponding nitro-derivative with tin and hydrochloric acid; on treatment with benzile in dilute alcoholic solution, *amidotriphenylethophenazonium hydroxide*,

$$NH_2{\cdot}C_6H_3{<}\begin{matrix}N{=}CPh\\ NPh(OH)\end{matrix}{>}CPh,$$

is produced; this is orange-yellow in colour, melts at 98°, and dissolves in water with a red colour; sulphuric acid produces a red coloration, which changes to green and then to red on dilution. The *ferrichloride* is deposited from alcohol in large, transparent, ruby plates.

By the action of benzile on triamidodiphenylamine,

$$C_6H_3(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$$

[$NH : NH_2 : NH_2 = 1 : 2 : 4$; $NH : NH_2 = 1 : 4$], a compound is formed which dissolves in water with a red colour; the solution in alcohol, ether, or benzene is yellowish-red, and shows no fluorescence; the base is amorphous, and has the formula

$$NH_2{\cdot}C_6H_3{<}\begin{matrix}N{=}CPh\\ N(C_6H_4{\cdot}NH_2)(OH)\end{matrix}{>}CPh;$$

it is related to the phenosaffranines. The *hydrochloride*, $C_{26}H_{21}N_4Cl + H_2O$, crystallises from water in dark-red plates.

Dimethyltriamidodiphenylamine, $C_6H_3(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$

[$NH : NMe_2 = 1 : 4$; $NH : NH_2 : NH_2 = 1 : 2 : 4$],

prepared from the corresponding dinitro-compound by reduction with tin and hydrochloric acid, also reacts with benzile; the resulting product crystallises readily, but has only feeble tinctorial powers.

J. B. T.

Action of Iodine on Thiobenzamide. By A. W. v. Hofmann and S. Gabriel (*Ber.*, **25**, 1578—1589).—By the action of iodine on thiobenzamide in alcoholic solution, a compound is formed which was believed to have the formula $S{<}\begin{matrix}CPh{:}N\\ CPh{:}N\end{matrix}$; the following results prove, however, that the substance is *dibenzenylazosulphime*, $S{<}\begin{matrix}N{=}CPh.\\ CPh{:}N\end{matrix}$

Attempts to synthesise the substance by the action of sulphur on benzalazine at 200°, and of hydrazine on thiobenzoic anhydride, were unsuccessful. On heating the thio-derivative with a mixture of glacial acetic acid and fuming hydrochloric acid for seven hours at about 230°, benzoic acid, ammonia, and sulphur are formed.

The compound $C_{14}H_{14}N_2$, which is prepared by the reduction of the

thio-compound, melts at 77—78°, instead of 71°, as previously stated (*Ber.*, **2**, 645), and proves to be *benzylbenzenylamidine*,

$$CH_2Ph{\cdot}NH{\cdot}CPh{:}NH;$$

it may be prepared from benzimidoether and benzylamine; on heating with hydrochloric acid at 180°, it yields benzyl chloride, benzoic acid, and ammonia, whilst, on heating the compound alone, it decomposes into benzonitrile, benzylamine, and kyaphenine.

The authors suggest that the diazothioles prepared by Hector (compare Abstr., 1890, 526) are really azosulphimes analogous to the above compound; they have prepared a diazothiole from methylphenylthiocarbamide, which crystallises from dilute alcohol, melts at 94—95°, and, on reduction with zinc and hydrochloric acid, yields methylaniline and other compounds, which are being further investigated.

The substance described by Gebhard as piperidinethiocarbamide (m. p. 92°) proves to be *piperidine thiocyanate*. J. B. T.

So-called Dibenzimidine. By A. Pinner (*Ber.*, **25**, 1624—1627). —The author has recently prepared difurylmethylcyanidine from furfuramidine and acetic anhydride (this vol., p. 1006), and finds that, in properties, it closely resembles "dibenzimidine," formed by the interaction of benzamidine and acetic anhydride; he has, therefore, caused new analyses of the latter compound to be made, and finds it to be *dimethylphenylcyanidine*, $CMe\lessgtr^{N{\cdot}CPh}_{N{:}CPh}\gtrless N$; this substance has, however, already been obtained by Krafft and v. Hausen by the action of aluminium chloride on a mixture of benzonitrile and acetic chloride, and has been termed by them methyldiphenyl tricyanide.

"Ditolenylimidine" and "β-dinaphthenylimidine" are, therefore, really *ditolylmethylcyanidine*, $C_{18}H_{17}N_3$, and *dinaphthylmethylcyanidine*, $C_{24}H_{17}N_3$, respectively. J. B. T.

Pseudopelletierine. By G. Ciamician and P. Silber (*Ber.*, **25**, 1601—1604).—Tanret's observations on pseudopelletierine are confirmed; it crystallises from light petroleum in colourless, prismatic plates, and is unacted on by nitrous acid. The *aurochloride* is deposited from water in pale-yellow crystals; the *picrate* crystallises from water in long, lustrous, yellow needles; the *mercurochloride* is crystalline and colourless. A pale-yellow precipitate is formed with phosphomolybdic acid, and with iodine, in potassium iodide solution, pale-brown needles are deposited. The *cadmioiodide* crystallises from water in colourless groups of needles; the corresponding *bismuth* compound is deposited in scarlet crystals; the *mercuroiodide* crystallises in small, pale-yellow plates.

The *methiodide*, $C_9H_{15}NO,MeI$, crystallises from dilute alcohol in small, colourless cubes, which remain unmelted at 280°, and readily dissolve in water. On heating the compound with potash, dimethylamine is evolved, and an oily substance is formed, which may be purified by extraction with ether and distillation with steam in acid solution; it has an odour resembling that of acetophenone, and

yields a compound with phenylhydrazine acetate which melts at 76—77°. J. B. T.

Cystin and Cysteïn. By K. Brenzinger (*Zeit. physiol. Chem.*, **13**, 552—558).—Cysteïn reacts with mercuric chloride, forming the compound $C_6H_{14}N_2S_2O_4Hg_3Cl_6$. This salt, when treated with ethyl iodide, yields *ethylcysteïn*, $C_3H_6NO_2{\cdot}SEt$, which forms nacreous plates and melts at 226—228°. Like phenylcysteïn, ethylcysteïn, when boiled with sodium hydroxide and Fehling's solution, is decomposed into mercaptan and ammonia. It is, however, more slowly decomposed than phenylcysteïn. By the use of alkalis, and also by nitrous acid, pyruvic acid is not obtained from ethylcysteïn, as this acid is so easily further changed.

Cystin forms a benzoyl derivative which is decomposed by hydrochloric acid into benzoic acid and cystin. With isocyanic acid, cystin forms an uramido-acid, which with the loss of water, easily passes into the corresponding hydantoïn.

A number of unsuccessful efforts to form cystin synthetically were made. W. D. H.

Nitrated Silk. By L. Vignon and P. Sisley (*Bull. Soc. Chim.* [3], **6**, 898—904).—When silk is immersed in ordinary nitric acid (sp. gr. 1·133) at 45° for one minute, and is subsequently washed in water, it is coloured intensely yellow, and the colour is unaffected by exposure to air and light, whilst it is deepened by the action of dilute alkali solutions. Nitric acid free from nitrous compounds does not cause this coloration, which is found to vary in intensity directly with the amount of nitrous compounds present, and with the temperature and specific gravity of the acid used. The deepening of colour by alkaline solutions is independent of their causticity, whilst the silk increases in weight and takes up a certain amount of the base.

Silk treated with a mixture of hydrochloric acid and sodium nitrite is coloured pale yellow; the colour is rapidly browned on exposure to air and light, or by the action of boiling water or alcohol, whilst cold alkaline solutions turn it reddish-brown. Silk which has been subjected to the action of nitrous acid, or of nitric oxide, in an atmosphere of carbonic anhydride, and subsequently well washed, is colourless, but is coloured a stable yellow by nitric acid. Nitric peroxide colours silk yellow at once. Silk heated with nitrous acid, and then oxidised with potassium permanganate and hydrochloric acid, is coloured exactly as by nitric acid (impure), from which it seems that the yellow coloration is dependent on the action of nitrous compounds, and subsequently of an oxidising agent.

The yellow colour is discharged by acidified stannous and chromous chloride solutions. Analyses of the nitrated silk show that about 2 per cent. of nitrogen is fixed in the reaction, probably, primarily, as the nitroso-group, which the further action of the nitric acid converts into the nitro-group, a carboxyl group being displaced. The properties of the product somewhat resemble Mulder's xanthoproteïc acid, but this contains more carbon and less nitrogen, and results from a more intense action. Sulphuric acid dissolves ordinary silk

gradually to a slightly coloured solution, whereas nitrated silk is converted into a pale-yellow, viscid mass. Aqueous potash dissolves ordinary silk in the cold, and nitrated silk on heating; neither solution is precipitated by dilution with water, and both evolve ammonia when heated. Both varieties of silk are dissolved by hydrochloric acid and by zinc chloride solution.

Ammoniacal vapours are evolved on distillation of each variety, and a carbonaceous residue is left. On ignition, nitrated silk burns more rapidly than ordinary silk. T. G. N.

Physiological Chemistry.

Fibrin Ferment. By C. A. Pekelharing (*Verhand. d. Kon. Akad. van Wetenschappen te Amsterdam, Tweede Sectie*, Deel **1**, No. 3, 1892).—In continuation of a previous research (this vol., p. 87), it is now found that the substance described as the zymogen of fibrin ferment is not a globulin, but a nucleo-albumin. It can be precipitated from plasma by dilute acetic acid. It is convertible into fibrin ferment by union with calcium. Other nucleo-albumins, called tissue fibrinogens by Wooldridge, will similarly yield the ferment by treatment with calcium chloride. Caseïnogen, also a nucleo-albumin, although it hastens the coagulation of solutions of fibrinogen, to which a calcium salt has been added, will not, like the "tissue fibrinogens," produce intravascular coagulation. W. D. H.

Coagulation of Blood. By A. Griesbach (*Centralbl. med. Wiss.*, 1892, No. 27).—Although accepting, in the main, the conclusions of Arthus and Pagès, and of Pekelharing, as to the part played by calcium salts in coagulation, the author believes that he has succeeded in showing the important part played by the amœboid cells of the blood, by the fact that reagents, like weak osmic acid, which fix these cells, prevent the blood from coagulating.

Experimenting with crab's blood, the conclusion arrived at is, that the material liberated from the cells is a nucleo-albumin. This originates from the cytoplasm, not from the nucleus. Lilienfeld's (*Archiv Anat. u. Physiol.; physiol. Abth.*, 1892, 115) recent work, in which he considers that the nucleus plays an important part in the process, is adversely criticised. W. D. H.

Calcium Salts and Coagulation. By S. Ringer (*J. Physiol.*, **13**, 300—308).—In contradiction to what was stated in a former paper (Abstr., 1891, 954), it is now found that calcium salts do not promote the heat coagulation of albumin. They, however, cause heat coagulation of alkali-albumin. In some solutions they act partly by lessening the alkalinity of the solution. They have, however, a further and more powerful action, for they precipitate alkali-albumin in strongly alkaline solutions. Whether they act by diminishing the

solvent power of the menstruum, or whether they alter the proteïd molecule, and so render it less soluble, is not yet explained.

W. D. H.

Plasma and Serum. By A. E. Wright (*J. Pathol. and Bacteriol.*, **1**, 120—122).—It is pointed out that in fluids which form fibrin slowly, the fluid squeezed out by the contracting clot is not serum in the true sense of the word, but plasma, from which only part of the fibrin has been deposited. When the clotting is very perfect in blood, as when it is induced by the addition of calcium chloride, the clot is large and not very retractile, and the serum obtained is small in amount. By receiving blood into sodium oxalate solution, coagulation may be wholly or partially stopped, according to the amount of oxalate used. To obtain a maximum of serum, a small quantity of oxalate, which produces partial decalcification, should be used. Serum thus obtained is susceptible of a secondary coagulation, but may be freed from fibrinogen entirely by heating to 60° and filtering. W. D. H.

Formation of Sugar and Lactic Acid in the Organism. By T. Araki (*Zeit. physiol. Chem.*, **16**, 453—459; compare Abstr., 1891, 1125, 1392).—Exposure of animals to a low temperature leads to the appearance of albumin, sugar, and lactic acid in the urine. This fact is confirmed by the present research on rabbits and dogs placed for some hours in snow. It is believed that it is explicable on the ground of insufficient oxidation processes. The administration of veratrine to frogs leads to the appearance of sugar and lactic acid in their urine. W. D. H.

Retiform Tissue. By R. A. Young (*J. Physiol.*, **13**, 332—334).—The fibres of retiform tissue, which are in great measure concealed by the cells that surround them, resemble the white fibres of areolar tissue in histological characteristics, and, in fact, in many situations, are continuous with them. Mall, however, has recently stated that they do not yield gelatin on boiling. It is pointed out that Mall's methods are not free from error, and, moreover, it is shown that it is perfectly easy to obtain small but weighable quantities of gelatin from the structures (mucosa of intestine, lymphatic glands) where the tissue in question occurs, care being taken that all areolar tissue is removed. W. D. H.

Acids of Butter. By E. Koefoed (*Bied. Centr.*, **21**, 202—204; from *Bull. acad. roy. danoise*, 1891).—The filtered butter (785 grams) was saponified with a solution of sodium hydroxide (200 grams) in water (500 c.c.), and when cold treated with a mixture of strong sulphuric acid (300 grams) and water (500 c.c.), and digested on a water-bath; it was then heated on a sand-bath until the solution was complete. This was done in a reflux apparatus and in an atmosphere of carbonic anhydride. The amount of fatty acids was 720 grams. After extraction with ether and evaporation of the ether, a residue was left consisting almost entirely of butyric acid (6 grams). The aqueous residue was distilled under 30 mm. pressure, and the distil-

late (54 grams) fractionally precipitated with silver nitrate; it was found to contain caprylic and caproic acids. The residue in the flask was dissolved in alcohol (500 c.c.) and recrystallised from alcohol. A crystalline mass (100 grams) was obtained. The united alcoholic filtrates were treated with acetic acid (30 grams) and an alcoholic solution containing lead acetate (600 grams). The precipitate was dried, and afterwards treated with hot hydrochloric acid and the free fatty acids added to a crystalline substance already obtained; the weight was now 314 grams. When distilled under 30 mm. pressure, the acids were found to be palmitic, myristic, lauric, and capric acids.

The filtrates from the lead precipitate were made alkaline with ammonia, when a semi-fluid lead salt separated, most probably containing oxyoleïc acid. The filtrate from this salt contained oleïc acid and a monobasic acid of the formula $C_{15}H_{28}O_4$.

The results show that the acids of butter, other than $C_nH_{2n}O_2$, are oleïc acid, an acid $C_{15}H_{28}O_4$, and, most probably, Gottlieb's oxyoleïc acid, $C_{29}H_{54}O_5$ (?). The acids of the composition $C_nH_{2n}O_4$ are normal constituents of butter, and include all those from C_4 to C_{18} which have an even number of carbon atoms. The acids $C_nH_{2n}O_2$ occur in the following percentage amounts :—Stearic acid, 2; palmitic acid, 28; myristic acid, 22; lauric acid, 8; capric acid, 2; caprylic acid, 0·5; caproic acid, 2; butyric acid, 1·5. N. H. M.

Presence of Myristic Acid in Ox Gall. By Lassar-Cohn (*Ber.*, **25**, 1829—1835).—In the preparation of cholic acid by the Mylius method (*Ber.*, **25**, 803), the foreign acids are separated by precipitation with barium chloride in a solution containing 20 per cent. of alcohol. The author has examined the mixed barium salts so obtained, and has separated from them myristic, palmitic, stearic, and oleïc acids. He finds about 0·004 per cent. of myristic acid calculated on the bile taken.

The following method of separation was employed:—The mixed barium salts from 100 litres of bile are boiled with water (6 litres) and sodium carbonate (400 grams). The mixture is filtered, the filtrate evaporated to dryness, the residue extracted with alcohol, and the alcoholic solution evaporated to dryness. 100 litres of bile yield 480 grams of the crude sodium salts. The sodium salts are dissolved in water and fractionally precipitated with barium acetate. The successive separations of barium salts are severally decomposed with hydrochloric acid, and the fatty acid separated from the aqueous liquor, dissolved in 90 per cent. alcohol, a little ammonia added, and fractionally precipitated with a 10 per cent. solution of magnesium acetate. The magnesium salts are decomposed with hydrochloric acid, and the free fatty acid crystallised from 70 per cent. alcohol.

The pure magnesium salt of the myristic acid may be more readily obtained by completely precipitating the crude sodium salts with barium acetate, decomposing the mixed barium salts with hydrochloric acid, and fractionally precipitating the acids so obtained with magnesium acetate in alcoholic solution. E. C. R.

Phosphoric Acid in Urine. By P. Carles (*J. Pharm.*, [5], **25**, 497—499).—In normal cases the urine in the bladder is distinctly acid in its reaction. This is due to gastric juice, sarcolactic acid from the muscles, hippuric, oxalic, and especially uric acid, formed by the oxidation of proteïds and the waste of organic tissue. Lastly, according to Bouchard, phosphoglyceric acid is also a factor of this acidity. These acids naturally occur in combination in the blood, and if they exist free in the bladder, this is due to their secretion by the kidney. Phosphoric acid is in the same case; it is found as a normal or alkaline phosphate in the vessels. There is no evidence that it is separated by the kidney in any other form; but in the bladder its base is shared amongst the other acids, and the phosphates become normal or acid. When the urine is voided, it comes under the influence of bacilli which transform urea, traces of proteïds, creatine, and other nitrogenous products into ammonium carbonate, and the phosphate gradually becomes basic again. In special cases the urine may become alkaline in the bladder. In analysing urine, it appears most rational to estimate the total phosphoric acid, noting the reaction of the urine at the moment of its secretion, or at the latest when delivered. J. T.

Catechol in the Urine of Hydrophobic Rabbits. By R. Moscatelli (*Virchow's Archiv*, **128**, 181).—In rabbits, during the hydrophobic state induced by the injection of Pasteur's material, it appears that the urine always contains a considerable quantity of catechol. W. D. H.

Action of Quinone and of Quinone Derivatives. By O. Schulz (*Chem. Centr.*, 1892, i, 413—414; from *Inaug. Diss. Rostock*). —The investigations deal with the action of quinone and some of its derivatives on animal substances and on the living organism.

With both α- and β-glutin, quinone appears to unite after several days to form strongly coloured substances, and a similar compound is obtained from egg-albumin, whilst in each case some quinol was formed. With hæmoglobin, quinone is first reduced to quinol, whilst the hæmoglobin is changed to methæmoglobin; some of the hæmoglobin is at the same time decomposed, and a quinonehæmatin compound is precipitated; the latter is a very permanent substance.

Subcutaneously injected, quinone does not act as a poison in every case. But when taken internally as a 0·6 per cent. solution in sodium chloride, the nervous system is immediately strongly affected. The intestinal canal is also strongly affected, food cannot be digested for some days, and is vomited unchanged again. The urine on the second day is dark brownish-green coloured, and contains both albumin and quinolglycuronic acid.

With fresh blood, trichloro- and tetrachloro-quinone cause the formation of methæmoglobin; the trichloroquinone acting the more energetically of the two.

With dogs, given in doses of 1·5—2·0 grams, both trichloro- and tetrachloroquinone cause violent purging, and in the case of tetrachloroquinone, tetrachloroquinol combined with glycuronic acid and

sulphuric acid is probably formed. They both act less energetically than quinone, probably because they are insoluble in water.

Dichlorodihydroxyquinone is partly reduced, probably to dichlorotetrahydroxybenzene; its action is principally on the kidneys.

Dichloramidohydroxyquinone is reduced first to dichlorodihydroxyquinone, and then further to dichlorotetrahydroxybenzene.

Toluquinone acts in like manner to quinone. J. W. L.

Soluble Naphthol Compound. By Stackler (*Compt. rend.*, **114**, 1027—1028).—The calcium salt of β-naphthol-α-sulphonic acid is obtained in a state of purity if care is taken to start with pure β-naphthol and to isolate perfectly the α- and β-modifications. It has been called *asaprol*. It is neutral, very soluble in water or alcohol, is not affected by heat, is not an irritant, is but slightly poisonous, and is tolerated by the digestive organs and passes rapidly into the urine.

Doses of 160 milligrams per kilo. of body weight injected every two or three days for 15 days, or doses of 66 milligrams injected every three or four hours for two months are well supported by rabbits. A dose of 285 milligrams per kilo. injected all at once is injurious, and 500 miligrams caused death in a few hours. In comparatively large quantity the compound prevents the development of various bacteria, including those of Asiatic cholera, typhoid, and anthrax.

When administered by ingestion to man in doses of 1 to 4 grains, it does not reduce, but often increases, the quantity of urine. It acts as an antipyretic in various infectious diseases, in typhoid, and in acute polyarticular rheumatism, and rapidly reduces the latter.

C. H. B.

Thymolglycuronic Acid. By F. Blum (*Zeit. physiol. Chem.*, **16**, 514—524).—If thymol is administered to human beings, it leaves the body partly by the fæces as such, and partly by the urine, appearing there as the chromogen of a green pigment, as thymolsulphuric acid, as thymolglycuronic acid, and as thymolquinolsulphuric acid. W. D. H.

Putrefaction of Milk. By H. Winternitz (*Zeit. physiol. Chem.*, **16**, 460—487).—Milk retards the putrefaction of proteïds, and thus causes delay in the appearance of the first and last product of the decomposition of the proteïd molecule. This is due to the lactose it contains, and is independent of the formation of lactic acid. In this way milk exercises considerable influence on putrefaction processes in the intestine leading to a lessening of ethereal hydrogen sulphates in the urine; it thus diminishes the splitting of proteïd food into products which are of no value, and are perhaps harmful to the organism.

The so-called "bromine-substance" is detectable in the intestine below the entrance of the pancreatic duct. In the upper intestinal regions it is the result of the ferment activity of pancreatin; in the lower regions, perhaps, of putrefaction organisms also. It is not present in the large intestine nor in the fæces, and, therefore, like

leucine and tyrosine, which originate simultaneously with it, it undergoes complete absorption by the walls of the small intestine.

W. D. H.

Treatment of Chlorosis by Hydrochloric Acid. By W. H. White (*Guy's Hosp. Rep.*, **48**, 1891).—Bunge, Hamburger, and others state that inorganic compounds of iron are not absorbed by the alimentary canal. Bunge considers that the utility of iron salts in chlorosis is due to their forming an insoluble sulphide, and this allows the organic iron compounds (hæmatogen) to be absorbed, which would otherwise be destroyed by putrefaction processes. Bunge also lays stress on the antiseptic action of gastric juice. In the present communication, five cases are described, which were, therefore, treated with hydrochloric acid. The results were negative, or at any rate the improvement was not greater than occurs when the treatment is simply rest with good food. They, however, rapidly improved on treatment with sulphate of iron. W. D. H.

A Case of Anthrax in Man. By S. Martin (*J. Pathol. and Bacteriol.*, **1**, 21—25).—In previous papers on anthrax in animals, the chemical poisons found in the blood and organs, or obtained by artificial cultures, were albumose and an alkaloïd. In the present case, which occurred in a man, the blood contained the base, but no albumose; the spleen contained albumoses, but only a trace of the base. The amount of the poisons compared with that found in sheep was small. Considerable quantities of both poisons were found in the urine of the present case. The kidney is thus the channel by which excretion of the poison takes place. There was also glycosuria, but this may have been an accidental concomitant.

W. D. H.

Mucin in Myxœdema. By W. D. Halliburton (*J. Pathol. and Bacteriol.*, **1**, 90—94).—It is believed that the term myxœdema is a misnomer, and that the increase of mucin found in certain cases is explicable on the ground of simple overgrowth of connective tissues. When these tissues are first formed they are always richer in mucin due to the preponderance of matrix than when later this is replaced by fibrous (colligenous) or adipose deposit. In the present paper, the estimation of mucin in the organs of a case of myxœdema is described; special attention is directed to the skin, which contained less mucin than normal, and the heart (especially the heart tendons of calves), which contained considerable excess. A number of normal hearts (human and sheep) were also examined. The following conclusions are drawn:—

1. The percentage of mucin in normal heart tendons, although variable, as in most connective tissues, is on the average greater than in other connective tissues, *e.g.*, skin = 0·38; skeletal tendons = 0·5.

The average percentage of mucin in normal human heart tendons is rather less than in those of the sheep, 1·03 : 1·35.

The percentage of mucin (1·7 to 1·9) in the cardiac tendons of myxœdematous patients, leaving out of account the present case, in all instances exceeds the normal mean of that in non-myxœdematous cases, but not very greatly.

4. It is most important to notice that such slight excess of mucin is by no means pathognomonic of myxœdema, as in three out of the nine non-myxœdematous hearts examined there was a similar slight excess in the percentage of mucin.

5. The present case, however, stands apart from these, the increase in mucin (5·2 per cent.) being so marked that there can be no mistake that we have here to deal with a condition of myxœdema, using the word in its literal sense. W. D. H.

Hæmatoporphyrinuria. By Sobernheim (*Deut. Med. Woch.*, June 16, 1892).—This condition, although often a result of sulphonal poisoning, is not invariably so. In a case of a boy suffering from enteric fever, which is described, it occurred, although no sulphonal was given. It probably originated from a hæmatoma in the rectus abdominis muscle. W. D. H.

Cobra Poison. By A. A. Kauthack (*J. Physiol.*, **13**, 272—299).—The albumose of cobra poison is best separated by extracting with water poison which had remained for a week under absolute alcohol. In its properties it closely resembles proto-albumose. Alkaloïds are absent. Light apparently does not impair its activity; very prolonged boiling is necessary for this purpose. Chlorine-water destroys its poisonous action completely, so also do caustic alkalis. Iodine trichloride, potassium permanganate, phenol, and pancreatin are less powerful in destroying the poison. Silver nitrate, mercuric chloride, lauric acid, and alcohol destroy the toxic properties of the poison by precipitating the albumose. Ammona, citric acid, and pepsin have very little anti-toxic power.

Experiments to establish immunity against cobra poison were wholly inefficient. Strychnine, recently recommended as a cure, is neither a chemical nor a physiological antidote.

Cobra poison does not contain a globulin, although certain observers have stated that it does. A substance with some of the properties of globulin and of heteroalbumose may be obtained after certain manipulations. It is regarded as an artificial product.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Absorption and Digestion of Fat Oils by Plants. By R. H. Schmidt (*Bied. Centr.*, 1892, 113—115).—Experiments with moulds (*Aspergillus*, *Penicillium*, *Mucor*, *Phycomyces*) growing in a solution containing grape sugar, almond oil, pure oleïc acid, and glycerol, in addition to the necessary inorganic salts, show that neutral fats as well as free oleïc acid are able to support the growth, but not glycerol. Fungoïd growths flourish in glycerol and the fatty acids, but absorb the first the most rapidly. Addition of ammonium tartrate increases the rapidity of growth. Solid fats and fatty acids serve well as food for such growths, and mosses absorb oil and oleïc

acid, and oil is also absorbed by many germinating plants, such as peas. E. W. P.

Development of Cereals. By A. Hébert (*Ann. Agron.*, **18**, 33—47).—The author discusses the results arrived at by Dehérain, Nantier, Meyer, and himself in the light of recent experiments and analyses, and especially bearing in mind the discovery of vasculose in the straw by Dehérain and straw gum by himself (compare Abstr., 1891, 1285). The first period of cereal growth after germination is that of root activity, during which nitrogenous compounds and minerals are largely assimilated. Tables are given showing the progressive fall in the percentages of these substances as the crop matures, and similar statements are true of tannins, gums, and vegetable acids precipitable by lead acetate. The next period is that of leaf assimilation, during which cellulose, vasculose, and straw gum are largely produced. Starch is *not* produced during this first period of assimilation, what was entered as such in older analyses being all carbohydrates producing a reducing sugar by hydrolysis with acids. The third period, or ripening, commences as soon as the stem has acquired strength and rigidity enough to support the spike, and consists in the assimilation of soluble carbohydrates in the leaves for transformation into starch in the grain. There is no store or reserve of starch or starch-producing material in the stem, as formerly supposed, and the production of starch and consequent value of the crop depend on leaf action still going on, and therefore on weather permitting of maintenance of vitality in the leaves. So it happens that in seasons characterised by a very dry July, like 1889 in contrast to 1888, for example, the normal quantity of starch cannot be formed, the crop is very short in weight, whilst the proteïds, having been stored up at an earlier period, are in excessive proportion to the starch in the grain. Thus in 1888 Paturel found in square-head Scholey wheat 12·63 per cent. proteïds to 77·20 per cent. starch; in 1889, 15·53. The yields were per hectare:—

	1888.	1889.	
Grain.....	34·84	29·22	metric quintals.
Proteïds	438·9	447·0	kilos.
Starch	2689·0	1808·0	„

In 1891 comparative analyses of the wheat plant were made at different dates, which can be summarised thus:—

Proteïds and Carbohydrates per hectare in Goldendrop Wheat, 1891.

	June 16.	July 3.	July 21.	Aug. 3.	Aug. 19.
	kilos.	kilos.	kilos.	kilos.	kilos.
Dry matter.....	183·97	3718·3	4922·8	4381·1	3832·2
Proteïds	140·2	216·9	?	267·2	220·0
Reducing sugars	48·9	103·6	130·8	39·3	30·8
Dextrin.....	9·9	62·9	192·1	85·0	53·7
Straw gum reckoned as xylose	334·4	792·2	1246·8	1852·5	1729·8
Starch.....	none	48·5	517·7	665·1	452·1

Between August 3, the date of full maturity, and August 19 there was a serious loss of weight, especially of starch, the quantities being—

	August 3.	August 19.
Weight of grain per hectare ..	895·7	756·7 kilos.
Proteïds in grain	114·7	94·6 ,,
Starch in grain	582·2	432·3 ,,

The yield of grain, about 9 metric quintals per hectare, was singularly small, and the ratio of proteïds to starch large, as in 1889. On August 13 this ratio was 12·81 per cent. : 65·30 per cent.; on August 19, 12·50 per cent. : 57·14 per cent. Small yields of cereals are therefore due to lack of starch, and this is due to want of leaf action during the later stages of growth. J. M. H. M.

Presence and Function of Phloroglucinol in Plants. By T. Waage (*Ann. Agron.*, **18**, 204—206).—In the course of his researches, the author has examined 185 different plants. The reagent used is a solution of vanillin in hydrochloric acid (0·005 to 4·0), a drop of which will detect 0·001 milligram of phloroglucinol. Gymnosperms are rich in phloroglucinol, monocotyledons and gamopetalous plants poor, and polypetalous plants have none. Woody plants contain more than herbaceous: the distribution is almost the same in roots, stem, and leaves. When cells containing this substance divide, the new cells contain it also, so that in making a longitudinal section one meets with lines or chains of these cells. As to the mode of formation of this substance, see a former paper by the same author (Abstr., 1891, 605).

According to the author, phloroglucinol is an accessory or bye product of plant growth. It is interesting as entering into the molecule of very complex substances, such as phloroglucides and phloroglucosides; it takes part in the formation of phlobaphenes and colouring matters such as anthocyanin and erythrophyll. Plants which contain tannin contain phloroglucinol also. J. M. H. M.

The Proteïds of the Oat Kernel. By T. B. Osborne (*Amer. Chem. J.*, **14**, 212—224; compare Abstr., 1891, 1285 and 1390).—The proteïds of the oat undergo great change in contact with water or sodium chloride solution. The substance extracted by direct treatment of ground oats with alcohol differs much in properties and composition from that extracted by alcohol after the ground oats have for some time had contact with water or with sodium chloride solution.

Direct treatment of the ground oats with sodium carbonate solution yields the same globulin as that obtained by direct treatment with hot sodium chloride solution, but different to that obtained by direct treatment with cold sodium chloride solution. Sodium carbonate solution also extracts another proteïd—the same as that yielded by direct extraction with dilute potash-lye—which again is distinct in composition from that obtained after the oats have been in contact with water. It is remarkable that all these transformations are the

result of the use of water or sodium chloride solution as contrasted with the use of alcohol, alkali, or heat, three agents known to suspend or destroy fermentation. The fact that the globulin extracted after treatment of the ground oats with alcohol has the same composition as that obtained by direct treatment with sodium chloride would indicate that alcohol temporarily suspends a fermentation which is induced by water or solutions of neutral salts.

It is probable that the primary proteïds originally contained in the oat kernel are the three following substances :—

	Alcohol-soluble proteïd.	Salt-soluble proteïd or globulin.	Alkali-soluble proteïd.
Carbon.....	53·01	52·19	53·56
Hydrogen....	6·91	7·00	7·09
Nitrogen	16·43	17·86	16·20
Sulphur.....	2·26	0·65	0·90
Oxygen.....	21·39	22·30	22·25
	100·00	10·000	100·00

Of the above substances, the alcohol-soluble proteïd forms about 1·25 per cent., the globulin about 1·5 per cent., and the alkali-soluble proteïd the remainder of the proteïds contained in the oat kernel, with the possible exception of extremely small amounts of proteose and acid-albumin. The latter two substances are very probably the results of change occurring during extraction, but the evidence on this point is not conclusive.

The three other proteïds, obtained evidently by the alteration of the primary proteïds, and probably through fermentation when the ground oats are subjected to contact with water or solutions of neutral salts, are as follows :—

	Alcohol-soluble proteïd.	Salt-soluble proteïd or globulin.	Alkali-soluble proteïd.
Carbon.....	53·70	52·34	52·49
Hydrogen....	7·00	7·21	7·10
Nitrogen	15·71	16·88	17·11
Sulphur.....	1·78	0·88	0·80
Oxygen.....	21·83	22·69	22·50
	100·00	100·00	100·00

G. T. M.

Influence of the Nature of the Soil on Vegetation. By J. Raulin (*Compt. rend.*, **114**, 1119—1122).—The author has grown potatoes (Early Rose) in the following kinds of soil :—A. A mixture of equal parts of B, C, D, and E. B. Turf soil containing 64 per cent. of humus. C. Soil containing 73 per cent. of limestone. D. Earth containing 47 per cent. of clay. E. Soil containing 75 per cent. of sand. One half (0·5 are) of each patch was treated with a quantity of chemical manure containing phosphoric acid (0·80 kilos.), nitrogen (0·70 kilos.) as ammonium sulphate, potassium (0·80 kilos.),

as sulphate, and plaster (1 kilo.). The potatoes were planted in April, 1891, and gathered in September. The weights of the resulting tubers are given in the following table :—

	With manure.	Without manure.
A.	203·40 kilos. per are.	148·00 kilos. per are.
B.	146·10 ,, ,,	57·90 ,, ,,
C.	125·90 ,, ,,	72·60 ,, ,,
D.	73·10 ,, ,,	25·00 ,, ,,
E.	43·50 ,, ,,	10·60 ,, ,,

Twelve lots of nine tubers each were planted in soils of widely varying composition in order to discover the soil of maximum fertility. This seems to consist of 2·64 per cent. of clay, 23·30 per cent. of humus, 67·20 per cent. of sand, and 6·86 per cent. of limestone.

W. J. P.

Pea-Nut. By L. P. Brown (*Exper. Stat. Record*, **3**, No. 1, 1891).—The yield of pea-nuts in the United States amounted to 2,700,000 bushels in 1889, and was still greater in 1890. Two kinds are cultivated, the white and the red; the latter ripen better because earlier. The following tables show (1) the percentage composition of nuts grown in Tennessee, and (2) the percentage composition of the ash :—

	Water per cent.	Per cent. in dry substance.				
		Proteïn.	Crude fat.	Non-nitrogenous extract.	Crude fibre.	Crude ash.
Pea-nut kernels (1888)	3·87	28·65	49·35	17·23	2·37	2·40
,, ,, (1889)	4·86	27·07	48·60	19·30	2·52	2·51
,, meal	10·64	49·63	6·33	31·67	6·06	6·31
,, hulls (1)	8·81	6·42	1·34	17·14	73·07	2·03
,, ,, (2)....	7·81	7·94	2·17	13·36	65·81	3·63
,, hay	7·83	11·75	1·84	46·95	22·11	17·04

	P_2O_5.	K_2O.	Na_2O.	CaO.	MgO.	SO_3.	SiO_2.
Kernels	38·90	39·85	2·85	4·11	1·83	10·40	0·20
Hulls	5·63	31·78	7·85	27·01	12·60	8·89	4·13
Leaves	4·85	15·00	7·26	50·77	10·89	3·57	5·60
Stalks	5·34	19·23	7·52	25·80	19·67	7·42	9·93

Good crops can only be obtained with carefully selected seeds, well tilled soil, and careful treatment of the plants. The pea-nut belongs to the richest of all known foods, the meal being equal to cotton-seed meal, but the hulls have only a slight manurial value. Pea-nut hay

is a nutritious food, and is a very suitable substitute for clover hay, especially for cattle. According to experiments in Virginia and North Carolina, a moderate amount of artificial manures and farmyard manure seem to be profitable ; a manure containing about 15 lbs. of nitrogen, 10 lbs. of soluble phosphoric acid, and 20 lbs. of potash per acre might be tried. N. H. M.

Fermentations of Farmyard Manure. By T. Schloesing (*Ann. Agron.*, **18**, 5—18).—In that part of a manure heap to which air has access, as the temperature is gradually raised by aërobic fermentations, a purely chemical oxidation sets in, which goes on with increased rapidity after the temperature has risen high enough to stop the fermentations by killing the microbes. Experiments in flasks traversed by a current of air at different temperatures, with cattle manure sterilised in some instances, and unsterilised or inoculated with bacteria in others, show that the bacterial fermentations go on with great energy, even at 72·5°, since at that temperature they yield more than 15 times the quantity of carbonic anhydride proceeding from purely chemical oxidation. At 81° the bacterial oxidation ceases, and the inoculated or unsterilised manure yields no more carbonic anhydride than the sterilised manure. No combustible gas is contained in the products of oxidation.

Similar experiments on the anaërobic fermentations of farmyard manure, made by substituting a current of nitrogen gas for air, show that methane is found amongst the products only at temperatures below 66°, and in presence of organisms. The carbonic anhydride produced is much less than in presence of air, but is greater when organisms are present than in the sterilised samples, and in the latter case is greater at 66° than at 52°. The following statistics of the fermentation at 52° in an atmosphere of carbonic anhydride of 124·4 grams of fresh manure may be cited as typical. The fermentation was allowed to proceed for two months, and furnished nearly 9 litres of gas ; the maximum evolution of gas, 16·3 c.c. per hour, being on the sixth day. The manure underwent no change in colour or in odour, and the straws were yellow and lustrous as at the commencement, but more friable. A little hydrogen (15·8 c.c.) was found in the first tube of gases, but the remainder consisted of 4217·5 c.c. CO_2 and 4577·4 c.c. CH_4, containing together 4·720 grams C, 6·033 grams O, and 0·819 gram H. The loss suffered by the manure was determined by analysis of the fresh manure and the residue, after drying in a vacuum, to be as follows :—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Minerals.
Before fermentation	12·67	1·653	10·70	0·453	3·69
After fermentation	7·92	1·125	7·08	0·392	3·79
Loss	4·75	0·528	3·70	0·061	0·10 (gain)

No nitrogen gas was found amongst the products of fermentation. The 61 milligrams of nitrogen lost were converted into ammonia,

actual determinations of ammonia showing an excess of 51·7 milligrams N in the products over that in the fresh material, due allowance being made for ammonia extracted by the vacuum drying. Thus there is considerable production of ammonia during the anaërobic fermentation, which ammonia is not fixed in organic combinations.

The oxygen contained in the carbonic anhydride evolved exceeds by 2·333 grams that contained in the dry, fresh manure; and the hydrogen in the methane, ammonia, and free hydrogen produced exceeds by 0·305 gram that in the fresh, dry manure. It follows from these excesses, and from the proportion of the oxygen to hydrogen (nearly 8 : 1), that water enters into the reaction and furnishes the oxygen and hydrogen necessary for the formation of carbonic anhydride and ammonia. J. M. H. M.

Analytical Chemistry.

Improved Pipette for Gas Absorptions. By A. H. Gill (*Amer. Chem. J.*, **14**, 231).—The author employs a simple gas pipette fitted with a rubber bag, after the manner of the pipettes in the Orsat gas apparatus, as furnished by Muencke. This is found to preserve the reagents better, and to have the additional advantage of being much more easily filled and handled. G. T. M.

Preservation of Solutions of Metaphenylenediamine and its Employment as a Reagent. By G. Denigès (*J. Pharm.* [5], **25**, 591—594).—Two grams of the hydrochloride is dissolved in 100 c.c. of ammonia in a stoppered flask, and 5 grams of powdered animal black is added to the solution. The whole is well shaken three or four times at intervals of an hour, and allowed to remain until next day. If the solution is not quite colourless, the shaking is repeated. The liquid can be preserved indefinitely over the animal black, and the portion withdrawn for use by means of a pipette can easily be seen to be quite limpid. To detect hydrogen peroxide, 1—2 c.c. of the reagent is heated to boiling during one minute with some drops of the liquid to be tested; in presence of the peroxide, a blue colour, more or less intense, is produced, which is perceptible after two minutes' boiling if the liquid only contains a few milligrams per litre. This coloration becomes red on the addition of soda or potash. For the detection of nitrous acid, 5 drops of the reagent is placed in a tube with 5 c.c. of 10 per cent. sulphuric acid; the mixture should not be coloured; 100 c.c. of the water to be tested is added, and heated to boiling during five minutes; a yellow colour, apparent on looking down the tube, indicates the presence of nitrites. The nitrites may be quantitatively estimated by adding nitrite solution of known strength to distilled water and comparing as in nesslerising.

J. T.

Estimation of Hydrochloric Acid in the Contents of the Stomach. By G. Langermann (*Virchow's Archiv*, **128**, 408—412). It is pointed out that most of the methods at present used for estimating the hydrochloric acid in the gastric juice only take into account the free acid; the chlorine, combined with proteïd matter, and the metallic chlorides should also be estimated in order to obtain more trustworthy results. The method recommended is that of Hayen and Winter (*Du chimisme stomacal*, Paris, 1891). Into each of three vessels, *a*, *b*, and *c*, 5 c.c. of the material to be tested is placed; excess of concentrated solution of sodium carbonate is added to *a*, and all three are evaporated on the water-bath; *b* is heated an hour longer to drive off all free hydrochloric acid; sodium carbonate is then added, and it is once more concentrated; *c* is dried, and then incinerated, and thus all combined (*i.e.*, with proteïd) chlorine is given off. All three are raised for a few minutes to a red heat when dry. The residues are taken up with distilled water, a little nitric acid is added, and the mixture boiled to drive off carbonic anhydride. The chlorine is estimated in each in the usual way by silver nitrate; *a* gives the total chlorine; *b* gives the fixed and combined chlorine; *c* gives the fixed chlorine only. The difference between *a* and *b* gives the value of the free hydrochloric acid. The difference between *b* and *c* gives the value of the combined hydrochloric acid.

W. D. H.

Estimation of Nitrogen. By V. Edwards (*Chem. News*, **65**, 241, 265). The use of an iron flask for the distillation operation in the Kjeldahl method is recommended as rapid, convenient, and advantageous; a small correction, however, has to be made owing to the absorption of a small amount of nitrogen from the air by the moist iron oxide, which is given off as ammonia during the distillation. For nitrates, the author employs the iron flask and 10 grams of zinc grains, 5 grams of iron filings, 0·5 gram of the nitrate, 100 c.c. of 30 per cent. solution of potash, and 50 c.c. of water; after an hour 100 c.c. more water is added, and the ammonia distilled off into standard acid. Blank determinations are first made with the iron filings for the reason stated above.

D. A. L.

Report on Phosphoric Acid. By W. B. Burney (*Chem. News*, **65**, 229—230; from the *Proc. of the 7th Annual Convention of the Association of Official Agricultural Chemists, Washington*).—In the first part of this report attention is drawn to Hundeshagen's molybdate method (Abstr., 1889, 762), to Hughes's suggestions relating to the analysis of concentrated superphosphates (*ibid.*, 1245), to Reitmair's results and views on the citrate method (*ibid.*, 1890, 416; 1891, 243), to the estimation of phosphoric acid in slags (*ibid.*, 1890, 290), and to its estimation in the presence of silica (*ibid.*, 1890, 825). During the past year, a sample of superphosphate and a sample each of a fertiliser with and without added organic matter were sent to various chemists for analysis; the results show great discrepancies, which are largely attributed to the carelessness of the operator, but, nevertheless, it is recommended that the American official method should be modified so that the washing of the phos-

phate, when estimating the water-soluble phosphoric acid, should be continued until there is 300 c.c. of filtrate, and in the estimation of the citrate-soluble phosphoric acid the solution should be filtered hot and rapidly, and the residue washed twice with half strength ammonium citrate and then with water at the ordinary temperature; whilst for the estimation of the total phosphoric acid, it is recommended to prepare the solution by the magnesium nitrate method when cotton-seed meal or other organic matter is present, but in other cases by the 30 c.c. nitric and hydrochloric acid method.

D. A. L.

Differences in the Determination of Reverted Phosphoric Acid by the American Official Method of Analysis. By C. Gibson (*Chem. News*, **65**, 209—210, 221).—Having observed serious discrepancies in the results obtained by different chemists in the estimation of reverted phosphate by the American official method, the author has investigated the matter, and observed that the variation in the character of the ammonium citrate solution could account for the differences. He prepared a solution of ammonium citrate, A, in careful accordance with the official directions, neutralising with ammonia until the solution showed no reaction with either very delicate red or blue litmus or with rosolic acid. Another solution, B, was made by adding ammonia to a portion of solution A until it showed a very faint alkalinity with delicate red litmus-paper, whilst a third, and strongly alkaline solution, C, was prepared according to the directions of H. Joulie. In the first series of experiments, calcium phosphate (South Carolina rock phosphate) was digested with each of these solutions, following the official directions with solutions A and B, and Joulie's directions with C, but digesting only half an hour and at the ordinary temperature. The second series of experiments was conducted in exactly the same way as the first, only the digestion was continued for one hour. The third and fourth series were the same as the first and second, but with aluminium instead of calcium phosphate. The mean numbers obtained with each of these solutions for the percentage of reverted phosphoric acid in the 1st and 2nd, and for the percentage of available phosphoric acid in the 3rd and 4th series of experiments, were as follows:—

	A.	B.	C.
1st series.....	0·913	0·746	0·746
2nd ,, ...	1·846	0·761	0·760
3rd ,, ...	19·77	31·66	26·91
4th ,, ...	31·39	34·73	34·73

But the aluminium phosphate could be almost completely dissolved in all three solutions, if sufficient time was given. The results show the efficiency of the alkaline ammonium citrate solution for the separation of soluble from insoluble calcium phosphate, but they also show that the American official method is not always to be trusted. Therefore the author suggests that that method should be modified to permit of ammonia being added to the ammonium citrate solution until a faint alkalinity is perceptible with red litmus-paper, and of

the digestion being continued for one hour at 65°. He further suggests that Joulie's ammonium citrate method, with or without the modification of weighing as magnesium pyrophosphate, should be recognised as an alternative method. D. A. L.

Action of Ammonium Citrate on High Grade Aluminium Phosphate. By H. A. Huston (*Chem. News*, **65**, 241—242; from the *Proc. of the 7th Annual Convention of the Association of Official Agricultural Chemists, Washington*).—To study the action of ammonium citrate on aluminium phosphate, a sample containing 45·46 per cent. of phosphoric acid, none being water-soluble, and 7·25 per cent. of silica, was submitted to various experiments by varying the conditions used in the American official method for available phosphoric acid. Firstly, the effect of increasing the time of digestion was tried, and 2 grams of phosphate digested with 100 c.c. of citrate solution yielded up 21·24 per cent. in half an hour, 31·70 in one hour, 36·92 in two hours, 40·80 in four hours, 41·00 in six hours, and 42·70 per cent. in 10 hours; secondly, employing the same quantities of materials and digesting for half an hour at different temperatures, it was found that 2·18 per cent. was dissolved at 40°, 5·52 at 50°, 21·24 at 65°, 32·90 at 75°, and 39·52 at 85°; whilst digesting different quantities of phosphate with 100 c.c. citrate solution for half an hour at 65° showed that 16·80 per cent. was dissolved from 0·5 gram, 18·26 from 1 gram, 21·24 from 2 grams, 23·22 from 3 grams, 24·66 from 5 grams, and 28·64 from 10 grams of the phosphate; this point is being further investigated. The next experiments were made to ascertain the effect of acidity or alkalinity. 2 grams of phosphate digested for 30 minutes with 100 c.c. of citrate solution, to which was added either citric acid or ammonia; the former decreased, the latter increased, the solvent action of the citrate solution (compare preceding abstract). D. A. L.

Estimation of Silicic Acid in Fluorides. By W. Hampe (*Chem. Zeit.*, **15**, 1521—1522).—The estimation of silicic acid in minerals containing fluorine is generally done by Berzelius' method, which is also the one employed by Rose, or by a process devised by Fresenius and Hintz. Berzelius fuses the substance with sodium carbonate, and estimates the silicic acid both in the aqueous solution and the insoluble residue. Fresenius and Hintz analyse cryolite by heating this fluoride with sulphuric acid in a leaden tube while passing a current of dried air, and condense the mixture of hydrogen fluoride and silicon fluoride in ammonia. The contents of the leaden tube are exhausted with water, and any insoluble residue fused with soda and further treated similarly to Berzelius' plan.

When dealing with a substance containing both silicic acid and fluorine, which is not readily decomposed by fusion with sodium carbonate or potassium hydroxide, or sulphuric acid, neither of these methods are applicable, although Fresenius' process might be improved by fusing the substance with potassium hydrogen sulphate in a platinum apparatus, which, however, would be difficult to construct.

The author has now devised a process for the estimation of silicic acid in strongly ignited alumina containing fluorine, which will be useful to those engaged in the aluminium industry. 1 gram of the substance is fused in a platinum crucible with 10 grams of dehydrated borax, which must be, of course, free from silicic acid. The bottom of the crucible is well lined with borax, the intimate mixture of the sample and borax is introduced, the whole well covered with borax, and then fused for about 20 minutes. The fused mass is poured into a platinum dish, the crucible in which the fusion took place is also put inside this, and the mass is then treated with hot water until it is completely disintegrated, which generally takes two days. 5 grams of ammonium chloride is now added, and the mixture heated until the smell of ammonia has nearly disappeared. The precipitate, consisting of silicic acid and aluminium borate, or, perhaps, calcium borate, is filtered through a platinum or india-rubber funnel and well washed. The filtrate is evaporated to dryness in a platinum basin, the residue is heated to a little above 100°, and then taken up with water. The liquid, which has an acid reaction, is rendered alkaline with ammonium carbonate, and the precipitate filtered off as before. The filtrate is again and again evaporated, &c., until no further precipitate is obtained. The joint precipitates are burnt with the filters, and the ash fused with four times the weight of sodium carbonate. From the alkali silicate so obtained, the silicic acid is separated in the usual way by evaporation with hydrochloric acid.

The author has confirmed the accuracy of the process by experimenting with made up mixtures of silicic acid and a large excess of pure cryolite. The silicic acid was practically recovered.

L. DE K.

Estimation of Silicic Acid in Fluorides. By F. REGELSBERGER (*Chem. Zeit.*, **15**, 1714).—The author has analysed a sample of calcined alumina containing 4·8 per cent. of fluorine and 0·73 per cent. of silica, according to the method described by Hampe (preceding abstract), and recovered 0·70 per cent. of silica. The process seems, therefore, well suited for technical purposes, although it is a pity that it takes such a long time.

The author will, in due course, publish the details of a process on which he is still engaged, and which is a modification of the one proposed by Fresenius and Hintz. The operation is conducted in a specially constructed platinum apparatus, and aims at a correct estimation not only of the silica, but also of the fluorine.

L. DE K.

Estimation of Carbonic Oxide by means of Cuprous Chloride. By L. DE ST. MARTIN (*Compt. rend.*, **114**, 1006—1009).—The solution of carbonic oxide in cuprous chloride solution seems to take place in accordance with the law of Dalton and the absorption formulæ of Bunsen. One treatment with the liquid does not remove the whole of the carbonic oxide from a gaseous mixture containing a small proportion of it. If, however, the gaseous mixture is agitated with four successive quantities of the cuprous chloride solution, and

the latter is boiled in a vacuum, and the expelled gas analysed, 98·1—98·4 per cent. of the carbonic oxide actually present is obtained. The treatment of the gas with cuprous chloride is effected in a flask provided with a stopcock, the copper solution being pumped out of this flask into the vessel in which it is to be boiled. The latter vessel is also provided with a stopcock, and the two are connected by india-rubber tube whilst the solution is being transferred.

C. H. B.

Volumetric Estimations and Analytical Separations by means of Potassium Ferrocyanides and Ferricyanides. By C. Luckow (*Chem. Zeit.*, **15**, 1491—1492).—The use of potassium ferrocyanide is somewhat restricted, as so many ferrocyanides are insoluble. For instance, in the important titration of zinc ores (compare this vol., p. 915), it is necessary to remove iron and other metals before titrating with the ferrocyanide. The author, therefore, has made an attempt to introduce ferricyanide instead. Having prepared a potassium ferricyanide free from sulphates and chlorides, it was found that this substance may be used in acid solutions even in presence of ferric oxide, and that no precipitates are formed in presence of mercuric, lead, manganous, uranic, and stannic salts.

These different properties of the two double iron cyanides render it possible to estimate some metals volumetrically in presence of one another, or to estimate them gravimetrically, as most ferricyanides may be readily filtered off. Zinc, for instance, may be accurately estimated either volumetrically or gravimetrically by means of potassium ferricyanide in its acetic or nitric acid solution, even in presence of lead, which may then be titrated in the filtrate with potassium ferrocyanide. Tin may be titrated by means of potassium ferrocyanide, even in presence of arsenic and antimonic acids, after the solution has been evaporated with oxalic acid and then mixed with a little dilute sulphuric acid.

The ferricyanide solution should give no coloration with a uranium solution, and no precipitate with a lead salt. If it should do so, it must be mixed with a little chlorine-water, and the salt recrystallised.

When titrating with ferrocyanide or ferricyanide, it is not possible to add the indicator straight to the liquid under examination, but use must be made of test papers. The indicator used must show either the disappearance of the last trace of the metal or else the slightest excess of the precipitant.

The author prepares his test papers as follows:—A moderately thick but dense and smooth kind of filter paper is cut into strips of 30 cm. in length and 15 cm. in width. Across the narrow part, at a distance of about 4 cm. from each other, stripes are made with the solution of the indicator, which consists of cupric acetate or ferric chloride, if ferrocyanide is used; or cobaltous or ferrous sulphate, when a ferricyanide is employed in the titration. When both are used in succession, a mixture of ferrous ammonium sulphate and ferric chloride is used.

When apparently enough of the ferrocyanide or ferricyanide solution has been added to the solution to be tested, a little drop is taken out

by means of a thin pencil and put at a distance of about 5 mm. from one of the stripes, when the reaction will make its appearance if the least excess is present.

The author recommends using for the titration not more than 30 c.c. of liquid containing about 0·15 gram of metal. The process may also be performed by adding an excess of the reagent and titrating this in the usual manner. But amongst the ferrocyanides, there are some, like the zinc, nickel, and cobalt salts, which are very difficult to filter off, although this presents no difficulty with mercury, lead, and silver salts. The ferricyanides are, however, more easily filterable. L. DE K.

Detection of Normal Carbonate in Hydrogen Alkali Carbonates. By G. PATEIN (*J. Pharm.* [5], **25**, 448—451).—Magnesium sulphate does not precipitate a normal alkali carbonate in presence of a hydrogen alkali carbonate if the normal salt does not exceed the amount required to form sesquicarbonate. A better reagent than magnesium sulphate is found in a very dilute alcoholic solution of phenolphthaleïn. A solution of pure hydrogen alkali carbonate gives no colour with phenolphthaleïn, or only a very faint rose tint disappearing on the addition of a few drops of carbonic anhydride solution; but the presence of traces of normal carbonate causes a decided rose coloration, which only disappears on the addition of an amount of carbonic anhydride solution proportional to the amount of normal salt present. J. T.

Analysis of Aluminium. By A. E. HUNT, G. H. CLAPP, and J. O. HANDY (*Chem. News*, **65**, 223—225, 235).—For general purposes, a solution containing 35 per cent. of hydrochloric acid, sp. gr. 1·2, is regarded as the best solvent for aluminium. To determine the total silicon, combined and uncombined, about a gram of the metal is dissolved in 15 c.c. of nitric acid, sp. gr. 1·2, and 2 c.c. of concentrated hydrochloric acid, another 2 c.c. of the latter acid being added as soon as the first action has ceased; when the metal is dissolved, the solution is stirred and rapidly evaporated with 20 c.c. of concentrated sulphuric acid until fumes of sulphuric anhydride appear, but is not allowed to spirt. When cool, 75 c.c. of water and 10 c.c. of hydrochloric acid are stirred in, the whole boiled for five minutes, the precipitate of silica and silicon collected, well washed with hydrochloric acid and water, ignited, fused with 3 grams of sodium carbonate or fusion mixture, decomposed with hydrochloric acid, then evaporated with 15 c.c. of strong sulphuric acid until sulphuric fumes appear. When cool, it is boiled up with 75 c.c. of water and 10 c.c. of hydrochloric acid, filtered, thoroughly washed, ignited, and weighed. The dehydration with sulphuric acid is not only rapid and efficient, but also leaves the silica in good condition for filtering. When both the combined and uncombined silicon are required, and inasmuch as the latter is found to suffer slight oxidation on ignition, any method involving burning filter papers becomes inadmissible for collection of the silicon and silica, and a platinum filter is suggested for the purpose, upon which the precipitate could be well washed, dried at 80°,

weighed, treated with sulphuric and hydrofluoric acids, washed, dried at 80°, and weighed again; the difference between the two weighings would be due to the silica, the last weighing being the silicon; the ratio of the silica to the silicon is less the more total silicon the metal contains.

For determining iron and copper, the hydrochloric acid solution is diluted, boiled, and saturated with hydrogen sulphide. The copper is determined by any method in the precipitate, the iron by titration with dichromate in the solution after boiling down. To estimate the aluminium, the hydrochloric acid solution, containing 1 gram dissolved in 25 c.c., is saturated, after the removal of the silicon and silica, with hydrogen sulphide, the copper sulphide filtered off and washed, the hydrogen sulphide boiled from the filtrate, and the solution made up to 250 c.c.; 50 c.c. of this is then nearly neutralised with ammonia, treated with 5 c.c. of a saturated solution of ammonium phosphate and 10 c.c. of a saturated solution of sodium thiosulphate, and boiled until free from sulphurous acid. After filtering and washing with hot water, the aluminium phosphate is redissolved in dilute hydrochloric acid, reprecipitated with slight excess of ammonia and a little ammonium phosphate, boiled, filtered, washed, ignited, and weighed as $AlPO_4$.

For the estimation of chromium in chromium-aluminium alloy, 2 grams of the alloy is treated with 50 c.c. of 10 per cent. potassium hydroxide solution, and the solution ultimately boiled and filtered. The residue, after burning the filter paper, is treated with 1 c.c. of concentrated sulphuric acid and 5 c.c. of hydrofluoric acid, evaporated until sulphuric fumes arise, then mixed with 4 grams of potassium hydrogen sulphate, fused for about 20 minutes at a low temperature, finishing over a blast to drive off most of the free acid; it is then cooled, rendered alkaline with sodium carbonate, some potassium nitrate added, the whole fused, dissolved in hot water, and filtered. The filtrate is warmed with ammonium chloride, filtered, the filtrate reduced with sodium sulphite or sulphurous acid, ammonia added, the chromium hydroxide redissolved in hydrochloric acid, diluted, reprecipitated with ammonia, well washed, and weighed as Cr_2O_3.

For the analysis of titanium aluminium, 2 grams of the alloy is dissolved in 50 c.c. of a 10 per cent. solution of potassium hydroxide, boiled for 10 minutes, diluted to about 125 c.c., boiled and filtered quickly, and washed 10 times with boiling water. The residue is ignited, crushed in an agate mortar, fused with 6 grams of potassium hydrogen sulphate, raising the temperature gradually and shaking the crucible round occasionally, finishing after 25 minutes with five minutes more at the full heat of the flame; when cool, the mass is brought to homogeneous fusion with 2 grams more of potassium hydrogen sulphate, and the fused mass is subsequently digested with water, and, if the residue is found to consist of silica only, it is rejected, if otherwise, it is again fused with potassium hydrogen sulphate. The filtrate is treated with ammonia to slight precipitation without re-solution, and the precipitate is dissolved by adding dilute sulphuric acid; the acid solution is diluted to 250 c.c. and saturated with sulphurous anhydride, it is then boiled gently for

three-quarters of an hour, more sulphurous acid is added to keep the iron in the ferrous state, the solution filtered, and the precipitate washed, ignited, and weighed as TiO_2. The iron in solution is precipitated with ammonia, redissolved in hydrochloric acid, and titrated with dichromate. D. A. L.

Estimation of Manganese by the Chlorate Method. By W. Hampe (*Chem. Zeit.*, **15**, 1579—1580).—The author strongly protests against a modification of his chlorate method which has been proposed by the Committee of the German Ironmasters' Association, and points out several defects in the Committee's mode of procedure, such as using impure chemicals, and working on far too small quantities of material. L. de K.

Estimation of Manganese by the Chlorate Method. By M. A. v. Reis (*Chem. Zeit.*, **15**, 1791).—The author attempts to justify the action of the Committee (see preceding abstract), and points out that, although Hampe's original process has been tried many times, it is now only used in two small works. The reason is not far to seek. Hampe's original process is attended with much evolution of unpleasant fumes, and there is often a loss through the violent bumping of the nitric acid and chlorate mixture. As modified by the Committee (use of a weaker acid and addition of the potassium chlorate all at once), no trouble is experienced in that direction. L. de K.

Colorimetric Estimation of Iron. By J. Riban (*Bull. Soc. Chim.* [3], **6**, 916—920).—In reference to the suggested employment of colorimetric methods to determine small amounts of iron in blood, the author publishes the results of numerous experiments made by him with Duboscq's colorimeter on the thiocyanate, acetate, and alkaline tartrate of iron, which prove the inaccuracy of the method to be due to the dissociation of these salts on dilution with water. T. G. N.

Nickel and Cobalt Reactions. By Terreil (*Bull. Soc. Chim.* [3], **6**, 913—916).—Solutions of nickel and cobalt salts are precipitated by hydrogen sulphide in presence of many organic salts, the precipitation varying inversely as the amount of free acid present. Oxalic acid and the oxalates are without effect, since these form insoluble oxalates which hydrogen sulphide does not decompose. Alkali sulphites, hydrogen sulphates, thiosulphates, phosphates, and pyrophosphates, even in slightly acid solutions, enable hydrogen sulphide to precipitate the metallic sulphides by double decomposition of the primarily formed nickel and cobalt salts.

On addition of a cold solution of sodium thiosulphate to a rose-coloured cobaltous solution, a blue coloration is produced, which, on subsequent dilution with water, is altered to pink. Warming, or spontaneous evaporation of the liquid, occasions the precipitation of cobalt sulphide, and the dry residue is completely transformed into sulphide on heating at 100—120°. Nickel solutions similarly yield a greenish-yellow solution, which rapidly deposits the sulphide.

On treating mixed solutions of nickel and cobalt with thiosulphate and then with alcohol, the solution forms two layers, the lower con-

taining crystals of the double salts. which, after well washing with absolute alcohol, may be distinguished by the nickel compound turning brown on exposure to the air, whereas the blue cobalt salt remains unaltered for some time. Sodium hypochlorite solution slightly acidified with hydrochloric acid precipitates cobalt sesquioxide after one or two minutes, and nickel sesquioxide after half to one hour, from their respective solutions. T. G. N.

Qualitative Test for Chromium. By L. W. McCay (*Chem. News*, **65**, 221).—The author points out that, when testing insoluble mixtures or salts for chromium by fusion with sodium carbonate and nitrate, some nitrite is formed, and passes into solution during the subsequent digestion of the fused mass with water. Consequently, when the yellow solution is acidified, it assumes, owing to the reducing action of the liberated nitrous acid, a greyish-blue colour, instead of the reddish-yellow colour set down by some authorities as the special indication of chromium in this test. D. A. L.

Molybdic Acid as a Reagent for certain Aromatic Hydroxy-compounds. By J. Stahl (*Ber.*, **25**, 1600—1601).—Ammonium molybdate or molybdic acid gives colorations ranging from yellow to dark-brown with aromatic orthodihydroxy-compounds, whilst with the corresponding meta- and para-derivatives, no coloration is formed.

The presence of bromo- or nitro-groups in the nucleus is without influence on the reaction, but ortho-, methoxy-, or ethoxy-compounds do not show any coloration.

Sodium tungstate behaves like ammonium molybdate.

J. B. T.

Estimation of Uric Acid. By A. Haig (*J. Physiol.*, **13**, 320—331).—The author defends his views and the process he has adopted (Haycraft's) against certain criticisms recently passed thereon (this vol., p. 365). W. D. H.

Detection of Sesame Oil in Olive Oil. By A. Gassend (*Chem. Centr.*, 1892, i, 459; from *Rev. internat. sci. fals. aliment.*, **5**, 98).—Some specimens of African olive oil give a red coloration with the sugar and hydrochloric acid test similar to that obtained with sesame oil. Spectroscopically, they are easily distinguished. Chemically, they may be distinguished by adding a little of a 10 per cent. solution of sodium hydrogen sulphite. The red coloration produced by olive oil is discharged very quickly, whereas that produced by sesame oil is not discharged for 12—40 minutes. J. W. L.

Detection of Vegetable Oils in Lard. By P. Welmans (*Chem. Centr.*, 1892, i, 417; from *Pharm. Zeit.*, **36**, 798—799).—The reaction depends on the presence of alkaloïds in the vegetable oils. To 1 gram, or 25 drops, of the lard is added 5 drops of chloroform and 2 c.c. of phosphomolybdic acid solution, together with a few drops of nitric acid, the mixture being well shaken. The presence of alkaloïds or of

glucosides causes reduction, accompanied by a green coloration. Purified oils do not react in this way.

Picric acid in ethereal solution, when shaken with 10 c.c. of the oil, gives, after allowing the ether to separate, a brown coloration.

J. W. L.

Estimation of Fat in Milk by Schmid's Method. By J. Pinette (*Chem. Zeit.*, **15**, 1833).—The author has slightly modified this process, and operates as follows:—10 c.c. of milk is heated in an Erlenmeyer flask with 10 c.c. of common hydrochloric acid until the caseïn has redissolved and the fatty drops float on the top. It makes no difference if small flakes of albumin remain undissolved; in fact, too long heating is injurious, as it causes charring of the fat. After cooling somewhat, the mixture is put into a burette which has a glass stopcock at the bottom and a glass stopper on the top. The flask is rinsed out several times with a mixture of equal volumes of ether and light petroleum, and this is introduced into the burette up to the top division. The ether being added to the still warm mixture suffers some evaporation, whereby the acid solution is rendered sufficiently cold. The burette is now closed and thoroughly shaken for some time, until one is sure that all the fat has passed into solution. The whole is now allowed to remain quiet until the ethereal layer has separated perfectly clear, which takes a longer time than in Röse's process. An aliquot part of the ethereal mixture is now pipetted off, evaporated in a weighed flask, and the fat is finally dried and weighed. If the ethereal layer is not quite clear, and contains small globules of water, it must, after pipetting off, be passed through a dry filter, but it is, of course, better to wait a while until it has become perfectly clear.

The process is very accurate and rapid. As the ethereal mixture can be readily recovered by distillation, it is also a very economical one.

L. de K.

Estimation of Fat in Yolk of Eggs. By S. Bein (*Bied. Centr.*, **21**, 138—139).—The average percentage of crude fat capable of being extracted from yolk of eggs by ether amounts to 30 per cent., but when one-tenth of salt is mixed with the yolk this percentage falls to 27, and after the mixture has been kept for 4—5 months the percentage further falls to 22—20. As salicylic acid and other preservatives exert no such reducing action, it is evident that salt forms some compound with the fat. The practical importance of this observation is great, for a loss of oil must also ensue in those manufactures, as of glove leather, where yolks are employed and are preserved in salt.

E. W. P.

Separation of the Xylenes. By J. M. Crafts (*Compt. rend.*, **114**, 1110—1113).—A sample of crude coal tar xylene boiling at 138—140° containing metaxylene (55—56 per cent.), paraxylene (21·5 per cent.), orthoxylene (9 per cent.), ethylbenzene (1·2 per cent.), and a little paraffinoïd hydrocarbon (0·8 per cent.), was analysed by the following process:—

The crude xylene (10—20 grams) is heated in a sealed tube

with concentrated sulphuric acid (2·5 parts) at 120° for an hour with continual agitation. A mixture (3—4 parts) of hydrochloric acid (1 part) and water (1 part) is then added, the unchanged hydrocarbon separated, and the heating with sulphuric acid repeated. The hydrocarbon subsequently separated is the paraffinoïd hydrocarbon insoluble in sulphuric acid. The acid liquors are now heated in a sealed tube at 122° for 20 hours; 97 per cent. of the metaxylenesulphonic acid is thus hydrolysed, and the hydrocarbon then measured. The acid mother liquors, on again heating in a sealed tube at 175° for 20 hours, liberate the ortho- and para-xylenes and the ethylbenzene. These are dissolved in sulphuric acid, and, on adding concentrated hydrochloric acid, paraxylenesulphonic acid, $2C_8H_9SO_3H,3H_2O$, crystallises out, and is filtered, washed with hydrochloric acid, dried, and weighed. The mixture (1 part) of orthoxylene and ethylbenzene is separated by treatment with bromine (20 parts) and iodine: under these conditions, the xylenes yield tetrabromides which are almost insoluble in ether and light petroleum, whilst ethylbenzene gives less highly brominated and more soluble substances. The metaxylene obtained by the above method crystallises at −51°.

Benzenesulphonic acid is not hydrolysed on heating its sulphuric acid solution with steam. Very pure toluene which does not crystallise at −95° may be prepared by heating its solution in sulphuric acid with steam at 160°. W. J. P.

Estimation of Creatinine in Urine. By J. Moitessier (*Bull. Soc. Chim.* [3], **6**, 907—908).—The author objects to the process of Gautrelet and Vieillard for the determination of creatinine in urine, which is dependent on the differential decomposition of urea, uric acid, and creatinine by alkaline hypobromite, both on account of the small amounts of nitrogen which the two latter compounds yield, and because lead urate is held in solution if an excess of lead subacetate is employed to remove the uric acid from the urine, and, again, creatinine is not completely precipitated from its dilute solutions by means of zinc chloride, as much as 90 per cent. being retained in solution, and even where Hoppe-Seyler's method is employed the author finds 70 per cent. is not precipitated. The only process which affords accurate and concordant results is that of Neubauer. T. G. N.

Estimation of Tannin. By G. Fleury (*J. Pharm.* [5], **25**, 499—500).—White of egg is dried at a moderate temperature and very finely powdered. This powder is washed with 10 per cent. alcoholised water faintly acidified with tartaric acid, and, when again dried, is preserved in a flask. The solution of tannin is placed in a flat-bottomed vessel with a weighed portion of the powder, seven or eight times the amount of tannin supposed to be present. The absorption takes 48 hours with frequent shaking; further, the solution should be acid. The solution is tested with ferric chloride. Finally, the powder is collected, dried at 100°, and weighed; a small sample of the powder is also dried and weighed at the same time. The tannin in nut galls cannot be determined by this method; the absorption is too slow. It is applicable to the tannin contained in

wine and in the petals of red roses. When gallic acid accompanies the tannin, its effect on ferric chloride must be considered, and it must be remembered that this acid is not absorbed. J. T.

Method of Analysis of Chlorophyllic Extracts. Nature of Chlorophyllane. By A. Étard (*Compt. rend.*, **114**, 1116—1118).—The author proposes to separate the colouring and other principles of plants by successive extractions with cold carbon bisulphide, alcohol, and alkalis. No definite results are given. W. J. P.

Estimation of Peptones in the Stomach Contents. By S. Riva-Rocci (*Chem. Centr.*, 1892, i, 344; from *Centr. Klin. Med.*, **12**, 897—899).—The total proteïds are first estimated by precipitation with absolute alcohol. In a second portion the amount of coagulable proteïds is determined by means of Devoto's method; and in a third portion the peptones are precipitated by means of magnesium sulphate and a little acetic acid. After weighing, the peptone precipitate is burned, 15 per cent. is added to the ash, and the difference is equivalent to the peptones. J. W. L.

Detection of Hæmatoporphyrin in Urine. By O. Hammarsten (*Zeit. anal. Chem.*, **31**, 233—235).—Owing, it would seem, to the increased use of sulphonal, cases of hæmatoporphyrinuria are becoming more frequent. The following is the method employed by the author for examining an urine in which the colour and spectroscopic characters indicated the presence of hæmatoporphyrin. The urine was first precipitated with barium acetate, and the filtrate from this precipitate treated with barium acetate and sodium carbonate alternately, until a filtered sample gave a white precipitate with these reagents. The precipitates were washed and extracted with acidified alcohol. The acid extract was shaken with an equal volume of chloroform and several times its bulk of water, when most of the colouring matter passed into the chloroform. This was rapidly withdrawn from the weak alcohol, washed well with water, and evaporated in shallow basins in the dark. The brown residue was soluble in chloroform with splendid purple colour, and could be crystallised from warm alcohol in needles resembling Nencki and Sieber's hæmatoporphyrin hydrochloride. It was insoluble in cold water and in highly dilute acids, sparingly soluble in cold alcohol, in these respects, and in the situation of the absorption bands, which were slightly nearer to the red end of the spectrum, differing from Nencki and Sieber's product (Abstr., 1888, 971). In only one case out of the four met with did the substance obtained appear to be identical with that of Nencki and Sieber; in another case the chromogen of a similar colouring matter was observed. Of the four absorption bands in the spectrum of a solution of hæmatoporphyrin in ammonia and zinc chloride, those between C and D, and between *b* and F disappear within 24 hours, the former first. The other two bands are permanent. M. J. S.

General and Physical Chemistry.

Behaviour of Optically Active Substances in Mixtures of Two Solvents. By E. Rimbach (*Zeit. physikal. Chem.*, 9, 698—708).—The substances used in this investigation were camphor and turpentine. Solutions of the former of different degrees of concentration in ethyl acetate and in benzene were first examined, and then solutions in mixtures of the two solvents were taken. Turpentine was examined in like manner in alcohol and in acetic acid and in mixtures of the two. In the case of camphor, it was found that with solutions containing about 50 per cent. the results obtained with the mixed solvents agreed with those calculated from observations with the simple solutions, on the assumption that the optical rotation is in no way influenced by mixing the two solvents. If the percentage of active substance is decreased, the calculated specific rotation is found to be somewhat smaller than the observed, the difference between the two being greater the less the amount of active substance present. The turpentine solutions behave in like manner, but in this case the differences between the observed and calculated values are so small as to fall very nearly within the limits of experimental error.

In order further to ascertain whether the presence of an optically inactive solid substance in a solution would produce the same effect as an optically inactive liquid, solutions of dextrose in water containing magnesium chloride and calcium chloride in different proportions were examined. In calculating the results, the inorganic salts were treated as playing the part of inactive solvents. Magnesium chloride is found to exercise practically no influence whatever on the rotation of dextrose solutions. The presence of calcium chloride, on the other hand, produces a considerable increase in the specific rotation, but the observed do not in this case agree with the above calculated values. The increase depends on the concentration of the salt solution, but is independent of the amount of dextrose present or independent of the concentration of the dextrose solution.

H. C.

Colour of the Ions. By W. Ostwald (*Zeit. physikal. Chem.*, 9, 579—602).—The author has investigated the absorption spectra of solutions of various series of coloured salts, measuring the position of the bands, and also photographing the entire spectrum. From his observations, it appears that the spectra of dilute solutions of salts with the same coloured ion are identical. For instance, the series of permanganates at a dilution of 500 litres gave the numbers (on an arbitrary scale) in table, p. 1138, for the absorption lines.

At this stage of dilution, then, at which the metallic permanganates are completely dissociated, the spectra of the solutions are identical, as may also be seen in the photographic reproductions, the spectra of the different salts being given side by side. Besides the permanganates,

Metal.	I.	II.	III.	IV.
1. Hydrogen	2601	2698	2804	2913
2. Potassium	2600	2697	2803	2913
3. Sodium	2602	2698	2803	2913
4. Ammonium	2601	2698	2802	2913
5. Lithium	2602	2700	2804	2914
6. Barium	2600	2699	2804	2914
7. Magnesium	2602	2700	2802	2912
8. Aluminium	2603	2699	2804	2914
9. Zinc	2602	2699	2802	2912
10. Cobalt	2601	2698	2803	2912
11. Nickel	2603	2700	2804	2913
12. Cadmium	2600	2700	2803	2913
13. Copper	2602	2699	2803	2913

the author studied the fluoresceïn salts, eosin salts, iodoeosin salts, dinitrofluoresceïn salts, orcinphthaleïn salts, and the salts of its tetrabromo-derivative, the salts of rosolic acid, of diazoresorcin, of diazoresorufin, the chromoxalates, safrosin salts, the salts of pararosaniline, of aniline violet, of chrysaniline, and of chrysoïdine. The results are in general the same as for the permanganates, any deviations being attributable to the formation of insoluble compounds, or to the hydrolysis of the salts of very feeble acids or bases.

J. W.

Physical and Chemical Phenomena at very Low Temperatures. By R. Pictet (*Compt. rend.*, **114**, 1245—1247).—By using powerful compressers and aspirators a mixture of sulphurous and carbonic anhydrides will give a temperature of −110°, nitrous oxide and ethylene will give about −150°, and air will give a minimum temperature of −210° to −213°. The low temperatures are measured with a dry hydrogen thermometer, and afterwards with thermometers containing alcohol or ether, these latter being verified by means of the hydrogen thermometer.

The author finds that the very long ether waves corresponding to very low temperatures pass readily through almost all bodies, and a vessel at −110°, for example, will cool with practically the same rapidity, whether it is enveloped in a layer of cotton wool 2 cm., 10 cm., or 50 cm. in thickness.

Very peculiar phenomena are observed in the solidification of chloroform. When immersed in nitrous oxide at −120°, the thermometer in the chloroform sinks to −68·5°, and crystallisation begins. If now the vessel is placed in sulphurous and carbonic anhydride at −80°, the thermometer falls to −80°, but the crystals of chloroform melt again. If put back into the liquid at −120°, the thermometer rises to −68·5°, and crystallisation begins again. At −83·5° the crystals remain stationary; if the temperature falls, they increase; if it rises, they melt. When the vessel is cooled at −120°, crystallisation takes place on the inner wall of the vessel, and it seems probable that the thermometer in the middle is affected by the latent heat of crystallisation, and at −68·5° is in dynamic equilibrium with the medium

in which it is immersed. At −80° no crystals are formed, and the thermometer is affected only by radiation. C. H. B.

Melting Points of Mixtures. By A. Miolati (*Zeit. physikal. Chem.*, **9**, 649—655).—The melting points of mixtures in all proportions of naphthalene (80°) with phenanthrene (96°), with diphenylmethane (25·6°), and with anthracene (213°) were determined. The results are given in tabular and curve form. The melting point of the pure substance is in all cases depressed by the addition of the foreign material, and falls until a minimum point is reached which is below the melting points of either of the constituents of the mixture. The position of the minimum apparently depends on the difference between the melting points of the substances present. If the two substances have nearly the same melting point, the mixture of lowest melting point contains the two in nearly equimolecular proportions. In other cases the minimum is always nearest to the melting point of the lower melting constituent. The depression of the melting point is in all cases approximately proportional to the number of molecules of the foreign material present, but as an examination of the curves expressing this relation shows, the proportionality is only approximate. H. C.

Heats of Combustion and Formation of Ethyl Alcohol, of Formic Acid, and Acetic Acid. By Berthelot and Matignon (*Compt. rend.*, **114**, 1145—1149).—The authors have re-determined the heats of combustion of ethyl alcohol, formic acid, and acetic acid by means of the calorimetric bomb, using all the precautions indicated by later investigations.

	Heat of combustion.		Heat of formation.		
	Constant volume.	Constant pressure.	Solid.	Liquid.	Dissolved.
	Cal.	Cal.	Cal.	Cal.	Cal.
Ethyl alcohol	325·1	325·7	—	69·9	72·4
Formic acid	62·8	62·5	+103·3	+100·8	+100·9
Acetic acid	209·4	209·4	+119·7	+117·2	+117·6

Heat of formation of gaseous formic acid at 100° = +96·0 Cal.; at 200° = +90 Cal. (approx.).

Heat of formation of gaseous acetic acid at 120° = 112·1 Cal.; at 250° = 107·1 Cal.

The formation of potassium formate by the action of carbonic oxide on potassium hydroxide is exothermic by reason of the heat of neutralisation of the formic acid by potash. The energy required for the decomposition of formic acid in presence of concentrated sulphuric acid is furnished by the hydration of the latter.

The decomposition of acetic acid into methane and carbonic an-

hydride will be exothermic above 250°, and in presence of an alkali will develop still more heat, because the carbonic anhydride formed will combine with two equivalents of alkali. C. H. B.

Dibromomalonic Acid. By G. Massol (*Compt. rend.*, **114**, 1200—1201).—This acid was obtained by the direct action of bromine on anhydrous malonic acid in presence of chloroform. It forms slender, silky, anhydrous needles, deliquescent and extremely soluble in water; heat of dissolution +2·02 Cal. *Potassium hydrogen dibromomalonate* forms brilliant, white, anhydrous crystals which are easily decomposed by heat; heat of dissolution −5·60 Cal. *Potassium dibromomalonate* forms a non-crystallisable mass which becomes anhydrous at 100° and decomposes at 120°; heat of dissolution −9·94 Cal.

$C_3O_4Br_2H_2$ diss. + KOH diss. = $C_3O_4Br_2HK$ diss.	develops	+15·49 Cal.
$C_3O_4Br_2H_2$ diss. + 2KOH diss. = $C_3O_4Br_2K_2$ diss.	,,	+29·44 ,,
$C_3O_4Br_2H_2$ sol. + KOH sol. = $C_3O_4Br_2HK$ sol. + H_2O sol.	,,	+37·00 ,,
$C_3O_4Br_2HK$ sol. + KOH sol. = $C_3O_4Br_2K_2$ sol. + H_2O sol.	,,	+32·18 ,,
$C_3O_4Br_2H_2$ sol. + 2KOH sol. = $C_3O_4Br_2K_2$ sol. + $2H_2O$ sol.	,,	+69·18 ,,

These values are about 10 Cal. higher for each acid function than the corresponding values for malonic acid. Similar differences have already been observed by Louguinine between acetic and trichloracetic acid. C. H. B.

Thermochemistry of Bibasic Organic Acids: Methylmalonic Acid and Methylsuccinic Acid. By G. Massol (*Compt. rend.*, **114**, 1373—1374).—The results obtained were as follows:—

Methylmalonic (isosuccinic) acid:—

$C_4H_6O_4$ sol. + KOH sol. = $C_4H_5O_4K$ sol. + H_2O sol.	develops	+28·16 Cal.
$C_4H_5KO_4$ sol. + KOH sol. = $C_4H_4O_4K_2$ sol. + H_2O sol.	,,	+20·76 ,,
$C_4H_6O_4$ sol. + 2KOH sol. = $C_4H_4O_4K_2$ sol. + H_2O sol.	,,	+49·12 ,,
$C_4H_6O_4$ sol. + 2NaOH sol. = $C_4H_4O_4Na_2$ sol. + H_2O sol.	,,	+40·50 ,,

Methylsuccinic acid:—

$C_5H_8O_4$ sol. + KOH sol. = $C_5H_7KO_4$ sol. + H_2O sol.	develops	+24·85 Cal.
$C_5H_7KO_4$ sol. + KOH sol. = $C_5H_6K_2O_4$ sol. + H_2O sol.	,,	+20·33 ,,
$C_5H_8O_4$ sol. + 2KOH sol. = $C_5H_6K_2O_4$ sol. + $2H_2O$ sol.	,,	+45·18 ,,

The heat of neutralisation of methylmalonic acid,

$$COOH{\cdot}CHMe{\cdot}COOH,$$

is practically the same as that of malonic acid, $COOH{\cdot}CH_2{\cdot}COOH$, and the heat of neutralisation of methylsuccinic acid,

$$COOH{\cdot}CHMe{\cdot}CH_2{\cdot}COOH,$$

is practically the same as that of succinic acid,

$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

The degree of separation of the two carboxyl groups is similar in the two members of each pair, and the results confirm the author's view that the heat of neutralisation is a function of the degree of separation of the carboxyls. C. H. B.

Glutaric (Normal Pyrotartaric) Acid. By G. Massol (*Compt. rend.*, **114**, 1437—1438).—Heat of dissolution, at about 20°, of glutaric acid −5·36 Cal., of anhydrous potassium hydrogen glutarate +13·73 Cal., of anhydrous potassium glutarate +4·57 Cal. The heats of neutralisation are as follows:—

$C_5H_8O_4$ diss. + KOH diss. = $C_5H_7O_4K$ diss. + H_2O	develops	+13·73 Cal.
$C_5H_7O_4K$ diss. + KOH diss. = $C_5H_6O_4K_2$ diss. + H_2O	,,	+12·65 ,,
$C_5H_8O_4$ diss. + 2KOH diss. = $C_5H_6O_4K_2$ diss. + $2H_2O$	,,	+26·38 ,,
$C_5H_8O_4$ sol. + KOH sol. = $C_5H_7O_4K$ sol. + H_2O sol.	develops	+26·70 Cal.
$C_5H_7O_4K$ sol. + KOH sol. = $C_5H_6O_4K_2$ sol. + H_2O sol.	,,	+17·53 ,,
$C_5H_8O_4$ sol. + 2KOH sol. = $C_5H_6O_4K_2$ sol. + $2H_2O$ sol.	,,	+44·23 ,,

These results confirm the author's previous conclusion that in the oxalic series the heat of neutralisation decreases as the molecular weight increases, and when they are combined with previous results (preceding abstract), they also confirm the conclusion that the heats of formation of salts of normal bibasic organic acids are lower than in the case of their non-normal isomerides. C. H. B.

Substitution of Radicles in union with Carbon and Nitrogen respectively: Explosives. By C. Matignon (*Compt. rend.*, **114**, 1197—1199).—The author has previously shown (this vol., p. 106; see also p. 4) that the substitution of an alkyl radicle in connection with nitrogen increases the heat of combustion by a greater quantity (163—165 Cal.) than the substitution of a radicle in connection with carbon (155—156 Cal.). In the second case, substitution is effected by the union of atoms of the same kind, but in the first case by the union of atoms of different kinds, and it seems probable that

this is the explanation of the difference in the thermal values, the exchange of valencies between different atoms involving a smaller loss of energy than a similar exchange between similar atoms.

With a view to decide this point, the behaviour of nitro-derivatives was investigated. In ordinary cases, the NO_2 group is united with carbon, and there is an exchange of valencies between dissimilar atoms. Berthelot has shown that the heat developed by this substitution has a mean value of +36 Cal.

From a thermochemical study of the nitroguanidine described by Thiele, the author finds that the heat developed by the substitution of NO_2 in this case is only +30·3 Cal. The nitro-group must be united with nitrogen, and it follows that the explanation suggested above will not hold good; for the introduction of NO_2 in connection with nitrogen increases the heat of combustion to a greater extent than the introduction of NO_2 in connection with carbon. It would follow from this result, however, that nitro-explosives containing the NO_2 group in connection with nitrogen should be more powerful than those in which this group is united with carbon. As a matter of fact, nitroguanidine explodes violently when small quantities are projected on to a heated surface. C. H. B.

Thermochemistry of Guanidine and Nitroguanidine. By C. Matignon (*Compt. rend.*, **114**, 1432—1434).—*Guanidine nitrate*:—Heat of dissolution at 10° = −10·15 Cal.; heat of combustion at constant volume (in calorimetric bomb) +207·8 Cal.

$$C + O_3 + H_6 + N_4 = CN_3H_5,HNO_3 \text{ sol. develops } +93{\cdot}5 \text{ Cal.}$$

Guanidine sulphate is obtained by the action of the calculated quantity of sulphuric acid on guanidine carbonate. It is very soluble in water, and crystallises with half a molecular proportion of water, which it loses at 110°. Heat of dissolution of the anhydrous salt at 10° = −6·75 Cal.

$2CN_3H_5,H_2SO_4$ diss. + $Ba(OH)_2$ diss. = $BaSO_4$ ppt. + $2CN_3H_5$ diss. + $2H_2O$ ..	develops	+ 5·8 Cal.
CN_3H_5 diss. + HNO_3 = CN_3H_5,HNO_3 diss.	,,	+14·12 ,,
CN_3H_5 sol. + HNO_3 sol. = CN_3H_5,HNO_3 sol.	,,	+32·1 ,,
$C + N_3 + H_5 = CN_3H_5$ sol.	,,	+19·2 ,,

The thermal value of the basic function of guanidine, +32·1 Cal., is intermediate between that of barium hydroxide, +31·7 Cal., and that of sodium hydroxide, +36·4 Cal. No thermochemical evidence could be obtained of the existence of a second basic function of the guanidine.

Nitroguanidine, obtained by Thiele's method, is very soluble in hot water, from which it separates on cooling in anhydrous, white needles. Its heat of combustion at constant pressure is +210·3 Cal., and hence its heat of formation from its elements is +22 Cal., and

CN_3H_5 sol. + HNO_3 liq. = $CN_3H_4{\cdot}NO_2$ sol. + H_2O liq.	develops	+ 30·3 Cal.

The heat developed by nitrification is lower than in the case of nitro-derivatives in which the nitrogen of the nitroxyl group is directly united with carbon (compare preceding abstract).

C. H. B.

Thermochemistry of Hydrazine and of Hydroxylamine. By J. Thomsen (*Zeit. physikal. Chem.*, **9**, 633—635).—Bach (this vol., p. 933) has commented unfavourably on the method of oxidation by means of silver nitrate, for the purpose of determining the heat of formation of hydroxylamine and of hydrazine. The author shows that the apparent want of agreement in the case of hydroxylamine rests on a misunderstanding, and is of opinion that water and nitrogen are not the only products of oxidation obtained from hydrazine and silver nitrate. J. W.

Formulæ for Calculating the Heating Power of Coal. By Scheurer-Kestner (*Compt. rend.*, **114**, 1269—1272).—The author quotes further examples to show that the actual heating power of coal cannot be accurately calculated from its percentage composition by means of Dulong's formula, the possible error being as much as 12 per cent.

Berthier's method of assay also gives results which differ widely from, and have no definite relation to, the results obtained with the calorimetric bomb. C. H. B.

Temperatures of Saturated Vapours of various Liquids under the same Pressure. By E. Colot (*Compt. rend.*, **114**, 653—654). The temperatures t and θ of the saturated vapours of any two liquids at the same pressure are connected by the linear equation

$$t = A\theta + B,$$

when A and B are constants for the particular liquids. The experimental values of these constants for 20 different pairs of liquids are given, and hold good for very wide ranges of pressure. The maximum error is 0·71°. Jn. W.

Viscosity of Liquids. By A. Handl and R. Přibram (*Zeit. physikal. Chem.*, **9**, 529—539).—The authors in this paper discuss the methods of calculation, &c., adopted by Gartenmeister (Abstr., 1891, 380), and uphold certain rules connecting the viscosity of liquids with their composition and constitution against objections raised by him. J. W.

Theories of Osmotic Pressure and of Electrolytic Dissociation. By M. Planck (*Zeit. physikal. Chem.*, **9**, 636—637).—The author upholds (against Arrhenius) his thermodynamical proof of the law for the lowering of the freezing point and of the vapour pressure of solutions, and disclaims any pretensions on his part to priority in the discovery of the electrolytic dissociation theory.

J. W.

Determination of the Electrolytic Dissociation of Salts by means of Solubility Experiments. By A. A. Noyes (*Zeit.*

physikal. Chem., **9**, 603—632).—According to the principles laid down by Nernst (*Zeit. physikal. Chem.*, **4**, 372), it is possible, from experiments on the solubility of a sparingly soluble salt in aqueous solutions of another salt containing one ion in common with it, to calculate the degree of dissociation of the one salt, provided that that of the other is known. The author has taken as his standard substance thallous chloride, which he assumes to be equally dissociated with the chlorides of the alkali metals in equally strong solution. Proceeding from this basis, he has calculated from solubility experiments the degree of dissociation for a large number of salts. His results are by no means in accordance with those derived from a consideration of the electrical conductivity of the salt solutions, as the following example shows:—

Percentage Dissociation of Potassium Chloride.

Concentration.	From conductivity.	From solubility.
0·016 normal	93·3	93·8
0·03 „	91·0	88·7
0·05 „	89·1	84·3
0·1 „	86·1	74·8
0·2 „	82·8	65·2

The chlorides of the alkali metals are equally dissociated, and the chlorides of magnesium, barium, calcium, manganese, zinc, and copper (cupric) are also nearly equally dissociated, the degree of dissociation being slightly less than in the case of the alkali chlorides. Cadmium chloride is much less dissociated than these. Thallous chloride forms with lead chloride an insoluble double compound having the formula $PbCl_2,3TlCl$. J. W.

Dissociation in Dilute Solutions of Tartrates. By R. v. Sonnenthal (*Zeit. physikal. Chem.*, **9**, 656—668).—While investigating the influence of concentration on the rotatory power of dilute solutions of certain normal and acid tartrates, the author found that although the specific rotation decreases in all cases with decreasing concentration up to a certain point, a change occurs as the solutions become very dilute, and the specific rotations begin to increase slowly and regularly with further dilution. This change takes place in the case of the neutral tartrates with solutions of about 0·3 per cent. to 0·4 per cent. concentration, and for the acid tartrates with the concentration 0·2 to 0·3 per cent. The occurrence and magnitude of the change depends on the nature of the metal or radicle present in the salt, the greater the atomic weight of the metal or molecular weight of the radicle, the more readily will the change take place, and the greater will be the influence of decreasing concentration. The change is also to a certain extent a function of the time, as freshly prepared solutions have a lower specific rotation than those which have been for some time prepared, the rotation increasing with the time that the solution has

been prepared until a certain limit is reached. The influence of time appears to depend solely on the solubility of the salt in water, as the above limit is reached more rapidly in the case of the more soluble salts than with those of lesser solubility. From the above facts, the author concludes that this change which takes place in the rotation of very dilute solutions of tartrates is due to dissociation of the salt molecules with rising dilution. H. C.

Interval of Change. By W. Meyerhoffer (*Zeit. physikal. Chem.*, 9, 641—648).—The author determines the solubility of the system $CuCl_2,2H_2O,2KCl$ + KCl, for temperatures from 0° to 90·5°. To represent the results the temperatures are taken as abscissæ, and as ordinates the ratios of the amounts of the two simple salts KCl | $CuCl_2$ in the saturated solutions. In this method of representation, the solubility curves of pure double salts appear as straight lines. The author formerly supposed that the curve for the solubility of the above system would cut the theoretical curve for the solubility of the pure double salt at low temperatures, but this is not found to be the case. With falling temperature the solubility curve for the system $CuCl_2,2H_2O,2KCl$ + KCl approaches the (theoretical) solubility curve for the double salt $CuCl_2,2H_2O,2KCl$, but at the temperature 39° a maximum is reached by the former, and the curves recede from one another on passing this point. This result would seem to show that a saturated solution of the pure double salt is incapable of existing at any temperature.

The author applies the above mode of representation to the results of Schreinemakers with the double iodide of potassium and lead, $PbI_2,2KI,2{\cdot}5H_2O$. For this salt there are two different intervals of change, the temperature at which water no longer decomposes the salt being reached in the one case with rising, and in the other with falling, temperature, the intervals being therefore positive and negative. The two curves cut one another at 69° where K_2I_2 | PbI_2 = 3·7. The system PbI_2 + $3{\cdot}7K_2I_2$, therefore, evidently exists in two different conditions of solubility. Other peculiarities of the curves are pointed out, and the author also criticises Trevor's work on the double sulphates of copper and potassium. H. C.

Polybasic Acids. By W. Ostwald (*Zeit. physikal. Chem.*, 9, 553—562).—From a study of the electrolytic conductivity of bibasic acids at different dilutions, it appears that in some cases the first replaceable hydrogen atom is split off as an ion almost entirely, before the second hydrogen atom begins to be attacked. In other cases the second replaceable hydrogen atom begins to come off when only about 50 per cent. of the first is dissociated. The author considers the phenomenon in connection with the behaviour of different polybasic acids with respect to indicators, pointing out that many feeble acids, such as sebacic acid, may be sharply titrated, while much stronger acids, such as phosphorous acid, give no sharp end point. The explanation he gives is as follows:—A bibasic acid, $R''H_2$, dissociates first into $\overset{+}{H}$ and $R''\overset{-}{H}$, which latter in its turn dissociates into

$\overset{+}{H}$ and $\overset{=}{R''}$. As the radicle R″H is already charged with one unit of negative electricity, which is associated with the atom to which the positive ion of the undissociated compound was attached, there will be more or less difficulty in effecting the introduction of a second negative charge into this radicle, according as this second charge is nearer or further from the first charge. Consequently, the nearer the charges of the bivalent ion $\overset{=}{R''}$ are to each other, the less will be the tendency of the second hydrogen atom to dissociate. But when two replaceable hydrogen atoms are near each other in the molecule, the acid is, *cæteris paribus*, a strong one, and when they are far removed from each other, it is a feeble one; so that there may often be a reluctance on the part of a moderately strong acid to dissociate a second hydrogen atom. The author illustrates his theory by means of numerous examples. J. W.

Chemical Equilibrium in Solutions. By G. Charpy (*Compt. rend.*, **114**, 665—667).—As a general rule, the additive character of the physical properties of mixed solutions holds only for low concentration, and one of the conditions necessary for the extended application of the additive property is that the particular property under consideration must be a linear function of the concentration. The density is such a property, for, by considering the density of solutions of ammonium, potassium, barium, and cupric chlorides as a function of the concentration, experimental results were obtained showing this function to be sensibly linear, the greater error being 1/40th of the molecular concentration in the case of copper chloride.

On making similar measurements with a mixture of potassium and sodium chloride solutions, it was found that the density could be represented as a linear function of the molecular concentration of one of the salts, the molecular concentration of the other being constant. Jn. W.

The Formation of Layers in Solutions of Salts in Mixtures of Water and Organic Liquids. By C. E. Linebarger (*Amer. Chem. J.*, **14**, 380—398; compare Abstr., 1888, 783).—Part I of the author's work deals with the behaviour of salts towards mixtures of water and methyl alcohol, ethyl alcohol, propyl alcohol, and acetone, respectively, as regards the formation of layers.

The organic liquid was added by degrees to a saturated solution of a salt in water contained in a test tube, with vigorous agitation, until either a layer formed or the salt was precipitated. A table shows the results when 70 typical salts were experimented with. From this, certain regularities in regard to the formation of layers are to be noted. Chlorides do not generally exhibit this phenomenon; the alkaline chlorides, however, form layers in a mixture of acetone and water, and, save lithium chloride, in a mixture of propyl alcohol and water. The smaller the molecular mass of the alkaline chloride, the less pronounced is the peculiarity of layer-formation. The reverse is true of the chlorides of the alkaline earths; here the smaller the molecular mass, the more readily does the layer-formation occur. The acetates and nitrates do not as a rule cause a separation into

layers. The sulphates and carbonates exhibit the peculiarity of layer-formation in the most marked degree. Taking the organic liquids into consideration, it is found that methyl alcohol forms layers only with potassium carbonate, and that when any salt forms layers in a mixture of ethyl alcohol and water, it does so also in mixtures of propyl alcohol and water and of acetone and water. It would thus seem that, the greater the molecular mass of an alcohol, the more pronounced the formation of layers. No such relationship can be detected between the alcohols and acetone. The layer-formation seems to depend upon the nature of the acid part of the salt and not upon that of the basic part.

Part II deals with the limits of the formation of layers under varying conditions of temperature and concentration. The upper limit of layer-formation, that is, the quantity of organic liquid present when a further addition of it prevents the layer from forming, was determined by adding successive small portions of the organic liquid to a certain volume of a titrated solution of the salt; the tube was shaken after every addition and the volumes of the layers noted after two hours. It was found that potassium carbonate is the only salt which is not precipitated by the solvent before this upper limit is reached. As a mean of two experiments, the upper limit for alcohol with 5·4 of water and 0·592 of potassium carbonate was 53·9. The lower limit, that is, the point where a layer ceases to form on account of the presence of excess of water, can be very accurately determined. A little of the organic liquid was run into a known volume of the titrated salt solution and enough water added to clear up any cloudiness; the bottle was then placed in a thermostat, and when its contents had acquired the desired temperature, enough of the organic liquid was added to produce a cloudiness. The bottle was then replaced in the thermostat and if the contents became clear a little more organic liquid was added. This was repeated until a *drop* of water would clear up the cloudiness caused by a drop or two of the organic liquid. The lower the temperature, the more water is necessary to bring about the disappearance of the layers; the temperature employed was 20°. The numbers obtained in individual experiments are given and represented in curves, but the author reserves discussion of them until he has completed his determinations of the composition of the layers. A. G. B.

Reaction of Hydrogen with Chlorine and Oxygen. By J. A. Harker (*Zeit. physikal. Chem.*, **9**, 673—697).—Dixon and the author have shown that, in contradiction to what was formerly held to be the case, hydrogen when exploded with oxygen and excess of chlorine does not unite only with the chlorine, but that water is formed at the same time. The experiments were, however, incomplete, and more particularly left quite undecided the question of whether the ordinary laws of mass action hold for this case as for others of gaseous combination. The author has, therefore, continued them with the view of elucidating this point. Great difficulty was at first experienced in the carrying out of the experiments, and special apparatus had to be devised, a full description of which is given in

the paper. The results comprise 18 experiments, in which the volume of chlorine added to 50 vols. H_2 and 50 vols. O_2 varied from 9·08 to 95·83. In all cases a division of the hydrogen between the chlorine and oxygen takes place. This division takes place in such a manner that the product of the number of molecules of hydrogen chloride and of those of oxygen divided by the product of number of molecules of water vapour and of those of chlorine is practically constant, the mean value of the constant taken from the experiments being 23. It, therefore, appears that the Guldberg-Waage law of mass action holds for this as for other cases.

H. C.

Equilibrium of Chemical Systems under Unequal Pressures. —By W. Spring (*Zeit. physikal. Chem.*, **9**, 744—745).—Remarks on a paper by Le Chatelier on the same subject (this vol., p. 937), in which the author claims priority for having shown that compression of solid substances beneath the surface of liquids will bring about their union far more readily than will compression of the dry material. H. C.

Hydrolysis of Substituted Ethyl Acetates. By P. C. Freer and F. L. Dunlap (*Amer. Chem. J.*, **14**, 366—376).—Ostwald has shown (Abstr., 1890, 818) that the substitution of a negative radicle for hydrogen in an acid increases the avidity of that acid. Thus in the three chloracetic acids there is an increase of avidity for each atom of chlorine :—Acetic acid, $k = 0·00189$; chloracetic acid, $k = 0·155$; dichloracetic acid, $k = 5·17$; trichloracetic acid, $k = 121$.

The authors find that a similar relationship exists in the rate of hydrolysis of the ethyl salts of these acids, that displaying the highest constant as determined by Ostwald being the most readily saponified.

The *modus operandi* was as follows :—The ethyl acetate was weighed in a small bulb, such a quantity being taken as could be saponified by 5 c.c. of a solution of barium hydroxide saturated at 15°. This bulb was dropped into a large test tube inserted in a Beckmann's apparatus for determining molecular weights by the cryoscopic method (Abstr., 1891, 784), and 75 c.c. of a diluent (equal parts of alcohol and water), having the same temperature as the bath, was added. After adding a few drops of phenolphthaleïn, the bulb was broken by a glass rod and the mixture stirred; 5 c.c. of the barium hydroxide solution were then run in from a burette, specially adapted to exclude carbonic anhydride, and the interval of time necessary for the disappearance of the colour of the indicator noted, together with the temperature of the bath. The experiments were repeated at different temperatures ranging from 0° to 60°, beyond which too much of the alcohol was volatilised. The results are given in detail and represented as curves; they show that, although the relationship between the times of hydrolysis at any given temperature is not similar to that obtaining between the avidities as developed by Ostwald, yet the same relative position is maintained, the ethyl salts

of those acids with the greatest avidities being most readily saponified. The results at 0° are here given:—

Ethyl chloracetate	84	minutes.
Ethyl dichloracetate	9·5	,,
Ethyl trichloracetate	7·5	,,
Ethyl bromacetate	90	,,
Ethyl dibromacetate	19·5	,,
Ethyl tribromacetate	17	,,

The introduction of the second chlorine or bromine atom exerts a much greater influence than that of the third.

It is found that an increase of temperature has a greater relative effect on the speed of hydrolysis of the mono-substituted than it has on the di-substituted acids; this is easily accounted for by the greater increase of velocity caused, among the lighter molecules, by an increase of temperature. A. G. B.

Spheres of Condensation and Evaporation. By O. Lehmann (*Zeit. physikal. Chem.*, **9**, 671—672).—The author points out that Beyerinck, in his paper on the "Action at a Distance of Aqueous Solutions on Water Vapour" (this vol., p. 956), has failed to notice a description of the formation of spheres of condensation in vapours around substances which are capable of absorbing these vapours, contained in the author's "Molekularphysik," i, 318 and 337. The formation of these spheres is similar to that of the spheres formed in solutions round growing crystals, and is due not to action at a distance, but to equilibrium being gradually established between absorption and evaporation in the sphere in question. H. C.

Studies on Energetics. By W. Ostwald (*Zeit. physikal. Chem.*, **9**, 563—578).—The author emphasises the fact that energy is the only magnitude common to all branches of physics, mass being confined, strictly speaking, to dynamics. He therefore proposes that in an absolute system of measurement, mass should be replaced as a fundamental unit by energy, so that all physical magnitudes should be expressed in terms of time, length, and energy. The following table exhibits the dimensions of various magnitudes in the old and new systems:—

	Old units.	New units.
Energy	$[ml^2t^{-2}]$	$[e]$
Mass	$[m]$	$[el^{-2}t^2]$
Momentum	$[mlt^{-1}]$	$[el^{-1}t]$
Force	$[mlt^{-2}]$	$[el^{-1}]$
Surface tension	$[mt^{-2}]$	$[el^{-2}]$
Pressure	$[ml^{-1}t^{-2}]$	$[el^{-3}]$
Power	$[ml^2t^{-3}]$	$[et^{-1}]$

Proceeding from the principle of virtual velocities, the author arrives at the following general energy principle, which may be applied to all branches of physics and chemistry:—

In order that a system containing any forms of energy may be in

equilibrium, it is necessary and sufficient that for every displacement of the system consistent with its conditions of existence, the sum of the quantities of energy which appear and disappear should be zero.

The author rejects the substantial existence of matter, and defines mass as the capacity of an object for energy of motion. J. W.

Apparatus for Hot Filtration. By T. Paul (*Ber.*, **25**, 2208—2210).—The apparatus consists of a glass or metal flask fitted with an air condenser and three side tubes. One side tube is used for introducing and withdrawing liquids. Of the other two side tubes, one takes the vapour of the liquid in the flask to the spiral jacket of the filter-funnel; the other takes the condensed vapour back into the flask. A tube splayed out at the top is fused into the inside of the neck of the flask between the two last-mentioned side tubes, and reaches to the bottom of the flask. This tube is closed at the lower end, but about 1 mm. up has a number of holes arranged in rings.

E. C. R.

Lecture Experiment illustrating the Effusion of Gases. By P. C. Freer (*Zeit. physikal. Chem.*, **9**, 669—670).—The apparatus, of which a sketch is given in the paper, consists of a U-tube of about 200 c.c. capacity, one limb of which is closed by a stopcock, and is graduated, the other limb being connected with a graduated tube, about 500 mm. in height, and of suitable bore. The stopcock communicates with a short tube which is drawn out to a fine capillary. The graduated limb of the U-tube is filled with the gas under examination, the other limb containing mercury. On opening the stopcock, the gas escapes through the capillary and the mercury falls, the time which the mercury takes to fall through a certain distance being noted, and the results with different gases compared. H. C.

Inorganic Chemistry.

Formation of Plastic Sulphur from Sulphur Vapour. By J. Gal (*Compt. rend.*, **114**, 1183—1184).—When sulphur vapour is condensed on the surface of a cold liquid such as water, dilute nitric acid, dilute hydrochloric acid, or a solution of sodium hydroxide, plastic sulphur is formed in thin, pale-yellow plates which under the microscope are seen to be formed of transparent, rounded grains. The plates consist of a mixture of soluble and insoluble sulphur; if heated at 100° for an hour, 13·6 per cent. remains insoluble in place of the 0·3 per cent. in the case of ordinary plastic sulphur, and 23 per cent. in the case of flowers of sulphur.

The proportion of insoluble sulphur in plastic sulphur formed from vapour varies with the conditions, and especially with the temperature of vaporisation. The percentage of insoluble sulphur at various temperatures above 200° is given in the following table.

Temperature.....	215°	230°	245°	260°	275°	290°	305°	320°
Per cent. insoluble.	18	22	25	28	31	34	36	37

C. H. B.

Formation of Sulphuric Acid by Burning Illuminating Gas. By E. Přiwoznik (*Ber.*, **25**, 2200—2205).—The author discusses the work of other authors on this subject. He has made experiments which show that sulphuric acid and ammonium sulphate are produced by luminous and non-luminous gas flames. By allowing the upper portion of a non-luminous flame to impinge on to the bottom of a platinum dish filled with water, a condensate is formed in concentric rings. The inner ring, which is about as big as a half-kreuzer, consists of ammonium sulphate. It is surrounded by a ring of sulphuric acid, and this by a ring of ammonium sulphate. The author supposes that the ammonia in the outside ring of the condensate is derived from the atmosphere. E. C. R.

Synthesis of Hydrogen Nitride. By W. Wislicenus (*Ber.*, **25**, 2084—2087).—The author has obtained hydrogen nitride by the action of nitrous oxide on ammonia in the presence of metallic sodium. Sodamide, $NaNH_2$, is first formed, and then breaks up into sodium nitride, sodium hydroxide, and ammonia. Potassium amide and zinc amide behave in a similar way. About $\frac{1}{4}$ to $\frac{1}{2}$ gram of sodium, in a porcelain boat, is put into a glass tube and cautiously heated in a stream of ammonia. When all the sodium is converted into amide, a current of dry nitrous oxide is passed over the product heated at 150—250° as long as ammonia is evolved. About 50 per cent. of the theoretical yield is obtained. The same reaction takes place when a mixture of ammonia and nitrous oxide is passed over melted sodium, but the yield is not so good, and small explosions take place. When zinc amide is employed, the yield is very poor. The hydrogen nitride was obtained from the product by the method described by Curtius (Abstr., 1891, 56), whose observations the author confirms.

The author is engaged in examining the action of other oxides on sodamide. E. C. R.

Action of Nitric Oxide on Metals and Metallic Oxides. By P. Sabatier and J. B. Senderens (*Compt. rend.*, **114**, 1429—1432).—The authors have investigated the action of nitric oxide on metals and metallic oxides at temperatures below 500°, or, in other words, below the point at which nitric oxide begins to decompose under the influence of heat alone.

Metals, such as silver and platinum, that do not oxidise when heated in air do not oxidise in nitric oxide. Mercury vapour is not oxidised at 450°, and aluminium remains unchanged. Oxidisable metals like copper, iron, cadmium, and zinc, whether fused or in the form of sheets, or even filings, are but superficially oxidised in nitric oxide even at a dull red heat. Lead, on the other hand, oxidises rapidly, and yields yellow litharge.

Metals obtained in a finely divided state by reduction in hydrogen

are, however, readily oxidised by the nitric oxide, but, as a rule, the products are different from those obtained by heating the same metals in air. Nickel at 200° becomes incandescent, and yields the greenish-yellow monoxide without any sesquioxide; cobalt at 150° becomes incandescent, and yields the maroon monoxide; iron at 200° yields the black monoxide, also with incandescence; copper at 200° yields homogeneous cuprous oxide with a cochineal-red colour, and the same oxide is obtained, with a brighter colour, at a dull red heat, the mass becoming incandescent. Palladium sponge, previously saturated with hydrogen, is not appreciably affected by nitric oxide in the cold, but at 200° it becomes incandescent, and the nitric oxide is completely converted into water and ammonia without any oxidation of the metal.

The behaviour of lower oxides, obtained, as a rule, by reducing higher oxides in hydrogen, was also examined. In many cases the products are different from those obtained by heating the same oxide in air. Yellowish-green manganous oxide, MnO, yields pale-brown Mn_3O_4; brown tungsten dioxide, WO_2, becomes incandescent below 500°, and yields the blue pentoxide W_2O_5; maroon uranium dioxide, UO_2, becomes incandescent below 500°, and is converted into the black oxide U_2O_5; molybdenum sesquioxide, Mo_2O_3, is converted with incandescence into the violet dioxide MoO_2; titanium sesquioxide, Ti_2O_3, yields the white titanic anhydride, TiO_2, without incandescence; stannous oxide below 500° becomes incandescent, and yields stannic oxide. Cuprous oxide and vanadium sesquioxide, V_2O_3, are not oxidised by nitric oxide. C. H. B.

Phosphorus Chloronitride and Phosphamide. By A. Besson (*Compt. rend.*, **114**, 1264—1267).—The formula $PCl_5,8NH_3$, previously ascribed to the compound of phosphorus pentachloride and ammonia (Abstr., 1891, 398), is confirmed by subsequent analyses. If this compound is slowly heated, it loses ammonia. Between 175° and 230° under a pressure of 50 mm. crystals sublime, and if this product is again sublimed under similar conditions, it has the composition PCl_2N. This compound is formed by the action of heat on the compound $PCl_5,8NH_3$, and does not pre-exist in it, for the latter does not sublime below 175°, whereas the chloronitride is distinctly volatile at 100° under reduced pressure. The chloronitride forms highly refractive crystals melting at 106°. The compound obtained by Gladstone $(PCl_2N)_3$ is a polymeride, and melts at 210°.

If after the expulsion of the chloronitride the heating is continued, ammonium chloride begins to sublime at 200°, and after heating at 250—300° for some time, a greyish-white residue of phosphamide, PNH_2, is left. If this is further heated in a current of nitrogen or simply in a tube closed at one end, it gives off ammonia, and the proportion of nitrogen in the residue gradually decreases. At a bright red heat in a vacuum, or in a current of nitrogen, the compound is completely decomposed with liberation of phosphorus.

Phosphamide is partially decomposed at the temperature (a red heat) at which, according to Gerhardt, it is formed, and the nitride

PN_2 described by Liebig and Wöhler does not seem to be the final product of the action of heat on the compound of ammonia and phosphorus pentachloride. C. H. B.

Amorphous Boron. By H. Moissan (*Compt. rend.*, **114**, 617—622). —A summary of the properties of pure amorphous boron. Boric acid is twice treated with less than the theoretical quantity of magnesium powder, and the product, on treatment with an acid, leaves amorphous boron.

Amorphous boron is a bright, maroon-coloured powder which stains the fingers, and can be compressed into a cake. Its sp. gr. is 2·45. It does not fuse at the temperature of the electric arc, but shrinks slightly and increases in density when heated to 1500° in an atmosphere of hydrogen. Its electrical conductivity is very low, the specific resistance being 801 megohms.

Boron takes fire in the air at 700°, and burns in oxygen with a brilliant green flame having little actinic power; in either case the combustion is soon stopped by the formation of a layer of boric anhydride on the surface of the boron. It combines energetically with sulphur at 610° to form a sulphide which is decomposed by water with evolution of hydrogen sulphide; it behaves in the same way with selenium, but does not combine with tellurium.

Boron burns in dry chlorine at 410°, and in bromine vapour at 700°, with the formation of boron chloride and bromide. It is dissolved by bromine water, and more readily by a solution of bromine in potassium bromide solution, but it does not combine with iodine.

It combines with nitrogen at 1230°, but not directly with phosphorus, arsenic, or antimony. Neither does it combine directly with carbon or silicon, although a boron carbide is formed when boron is heated in the electric arc in an atmosphere of hydrogen.

The alkali metals have no action on boron, but magnesium combines with it at a red heat. Iron and aluminium form borides only at high temperatures, whilst silver and platinum combine with it quite readily.

Acids react energetically with boron; sulphuric acid is reduced at 250°; the action of nitric acid is so vigorous as to raise the temperature to incandescence; phosphoric anhydride is reduced to phosphorus at 800°; arsenious and arsenic acids are reduced to arsenic at a dull red heat; iodic acid in solution is reduced to iodine in the cold, and a mixture of the dry acid with boron becomes incandescent, and iodine is evolved; chloric acid is reduced to chlorous acid.

The hydracids react with greater difficulty. Hydrogen fluoride is not attacked until a dull red heat is reached, when boron fluoride is formed and hydrogen liberated. Hydrogen chloride is attacked only at a bright red heat, whilst its aqueous solution has no action whatever on boron.

Sulphurous anhydride is reduced to sulphur at an incipient red heat. Steam is not attacked until a full red heat is attained, but the action, once started, proceeds with great energy, boric acid being formed and hydrogen set free. Carbonic oxide is reduced to carbon at 1200°. Silica is reduced to silicon when heated in a forge. Nitrous oxide is

decomposed by boron at a dull red heat, boron nitride and boric acid being formed; nitric oxide is not affected by it.

Metallic oxides are more readily reduced by boron than by carbon. When, for instance, a mixture of boron and cupric oxide is heated in a glass tube, the reaction which ensues is so violent as to melt the glass. Stannous oxide, litharge, antimonious and bismuth oxides are all readily reduced. A mixture of boron and lead peroxide detonates violently when triturated in a mortar. Ferric and cobaltous oxides are reduced at a red heat, but the oxides of the alkaline earths are not affected. Hydrogen is liberated by boron from fused potassium hydroxide. A mixture of boron, sulphur, and nitre deflagrates at a dull red heat, whilst small quantities of boron projected into fused potassium chlorate burn with a most dazzling flame.

Boron acts very energetically on the metallic fluorides; it decomposes the fluorides of the alkalis and alkaline earths at a bright red heat; zinc fluoride at a dull red heat, boron fluoride being formed; and it acts with even explosive violence on lead and silver fluorides. Its action on the metallic chlorides is not so energetic. The chlorides of the alkalis, the alkaline earths, zinc, and lead are not attacked at a red heat, but mercurous chloride is reduced to mercury at 700°. Lead, zinc, cadmium, and copper iodides are not reduced by boron, but tin and bismuth iodides are reduced with facility. Potassium, sodium, calcium, and barium sulphates are reduced by boron at a red heat to the corresponding sulphides.

Notwithstanding its great affinity for oxygen, boron may be immersed in fused potassium nitrate without any reaction occurring, provided that the temperature is below that at which oxygen is disengaged. Fused potassium nitrite, however, is decomposed by it with great violence. Sodium carbonate is reduced at a dull red heat, potassium carbonate at a somewhat higher temperature, and calcium and barium carbonates not at all.

The arsenites, arsenates, and chromates are all reduced at a dull red heat.

Boron behaves also as a reducing agent in the wet way. It reduces potassium permanganate solution, partially in the cold, entirely on heating. It reduces ferric chloride to ferrous chloride. It precipitates silver from silver nitrate solution in fine crystals, and reduces palladium, platinum, and gold from solutions of the chlorides of these metals.

Boron thus combines with the non-metals much more readily than with the metals. It is a more powerful reducing agent than either silicon or carbon, and on the whole is most nearly allied to the latter element. Jn. W.

Boron Iodide. By H. Moissan (*Compt. rend.*, **114**, 622—623).—A criticism of Besson's work (this vol., p. 771). The "active boron" of that author is probably a mixture of iron and sodium borides. A question of priority is also discussed. Jn. W.

Behaviour of Molecular Compounds on Dissolution. By G. Bodländer (*Zeit. physikal. Chem.*, **9**, 730—743).—If a solution of silver

chloride in aqueous ammonia is brought to crystallise by evaporation, silver chloride alone separates out, owing to a portion of the ammonia which holds the salt in solution being carried off along with the water. If, on the other hand, a concentrated solution of ammonia, containing at least 8·5 per cent. NH_3, is heated in a closed vessel with excess of silver chloride, and the clear solution then cooled, crystals separate out which differ altogether in appearance and properties from those of silver chloride. Similar crystals can be obtained by the addition of alcohol to a concentrated aqueous solution of silver chloride in ammonia. These crystals begin to decompose as soon as they are removed from the solution, losing ammonia and leaving nothing but silver chloride behind. The determination of their composition is therefore attended with some difficulty, but by analysing the solution from which they were separated, and thus determining the amounts of silver chloride and ammonia which had been removed, their composition was found to be $2AgCl,3NH_3$.

The solubility of silver chloride in water containing ammonia is known to depend on the amount of ammonia present, and at first increases very rapidly as more and more ammonia is added. When the solution, however, contains about 5 gram-molecules of NH_3 per litre, the solubility of the silver chloride is found to have reached a limit, and on further increasing the amount of ammonia very little more goes into solution. This fact may be explained by assuming that this point corresponds with a saturated solution of $2AgCl,3NH_3$, and if this is the only soluble compound formed by silver chloride and ammonia, it is evident that the saturated solution would be incapable of taking up more silver chloride. The compound $2AgCl,3NH_3$, is quite insoluble in alcohol, and silver chloride therefore does not dissolve in alcohol containing ammonia.

If lead acetate is added to a solution of silver chloride in aqueous ammonia, a precipitate of lead chloride is formed; potassium iodide causes a precipitate of silver iodide, and ammonium sulphide throws down silver sulphide. It therefore appears that the silver and chlorine in this compound are present as free ions, and that the compound is not a complex salt but a true molecular compound. This view is further confirmed by the determination of the reduction of the freezing point of water by this compound. The molecular reduction is found to be two to three times greater than the normal 18·5, and therefore decomposition of the substance must have taken place on solution. This decomposition cannot be into the constituents NH_3 and $AgCl$, as in this case the silver chloride would have separated from the solution, and can therefore only be electrolytic in character and due to the dissociation of the $AgCl$ into its ions. This view is confirmed by the determination of the molecular conductivity of the compound, the values of Van't Hoff's coefficient i obtained in this manner agreeing with those calculated from the reduction of the freezing point. A further confirmation is obtained from the fact that the addition of NH_4Cl or $AgNO_3$ reduces the solubility of the compound $2AgCl,3NH_3$ in water, in accordance with Nernst's law of the influence of the presence of one of its ions in solution on the solubility of an electrolyte. It is evident, therefore, that the com-

pound $2AgCl,3NH_3$ is a true molecular compound which undergoes electrolytic dissociation, but does not decompose on being dissolved in water.

The very small solubility of silver bromide in aqueous ammonia prevents the preparation of a crystalline compound of the two, but from the similarity in the behaviour of silver bromide towards solutions containing varying amounts of ammonia, the formation of a compound similar to that above described is highly probable.

H. C.

Strontium Phosphates. By L. Barthe (*Compt. rend.*, **114**, 1267—1269).—Normal strontium phosphate is obtained by adding a cold ammoniacal solution of 90 parts of crystallised sodium phosphate to a cold ammoniacal solution of 100 parts of crystallised strontium chloride, both quite free from carbonate. The precipitate is colloïdal and has a bluish tinge; after drying at 100°, it is anhydrous.

Distrontium hydrogen phosphate is obtained by adding a slightly acid solution of 70 parts of crystallised strontium chloride to a similar solution of 100 parts of crystallised sodium phosphate at a temperature not exceeding 50°. It is at first gelatinous, but gradually becomes granulo-crystalline. When heated in a gas and air blowpipe, it yields the pyrophosphate, $Sr_2P_2O_7$, which has a bluish tinge.

Strontium dihydrogen phosphate, $SrH_4(PO_4)_2 + 2H_2O$, is obtained by mixing equal volumes of decinormal solutions of phosphoric acid and strontium hydroxide at any temperature between 15° and 100°. If a cold solution of distrontium phosphate in phosphoric acid is concentrated at a temperature not exceeding 50°, it yields nacreous tabular crystals of the composition $2SrO,H_2O,3P_2O_5 + H_2O$, soluble in water. If the temperature exceeds 50°, the composition of the product varies; it is only slightly soluble in water. The strontium dihydrogen phosphate is obtained in spherical masses of crystals by diluting 10 grams of 50 per cent. phosphoric acid with 90 grams of water, allowing it to remain in contact with excess of distrontium hydrogen phosphate for 24 hours, filtering, and allowing the solution to evaporate spontaneously under a bell jar for several weeks.

C. H. B.

Basic Zinc Nitrates. By J. Riban (*Compt. rend.*, **114**, 1357—1358).—When pure zinc is dissolved in nitric acid diluted with about its own volume of water, zinc nitrate is first formed, but if the solution is boiled with excess of the metal, a white, basic salt separates, and if the liquid is filtered and allowed to cool, it gradually deposits further quantities of a basic salt. The first portion of the deposit from the filtrate consists of a mixture of tabular and acicular crystals, whilst the last portion consists of very short needles in stellate groups, of the composition $6ZnO,N_2O_5,8H_2O$.

The salt crystallising in plates can be separated from the acicular crystals by dissolving the mixture in the mother liquor, or, better, heating it with the mother liquor in sealed tubes at 150° for several hours. It then separates in nacreous lamellæ of the composition

$6ZnO,N_2O_5,7H_2O$. They belong to the rhombic or monoclinic system, and are almost insoluble in cold water. C. H. B.

Cadmium Hydrosilicate. By G. Rousseau and G. Tite (*Compt. rend.*, **114**, 1262—1264).—The layer that forms on the inner surface of the glass tubes in the preparation of basic cadmium nitrate is freed from the cadmium salt by treatment with alcohol, and is removed from the glass by prolonged treatment with warm water. It forms long scales which, when rubbed between the fingers, break up into microscopic needles, showing longitudinal extinction in parallel light. It has the composition $2CdO,2SiO_2,3H_2O$, and is soluble in hydrochloric acid with separation of pulverulent silica. At a dull red heat it loses very little water, but when heated to orange-redness it melts and then intumesces in consequence of the escape of water. If the heating is continued, cadmium oxide is volatilised, and after prolonged heating a residue of silica alone remains. It would seem that the presence of water is essential to the stability of the molecule.

It is singular that the only two metals which have formed silicates during the preparation of basic nitrates, namely, silver and cadmium, are also the two that hitherto have not yielded any definite silicates. The silver compound is a nitrosilicate (this vol., p. 684), but the cadmium hydrosilicate and basic cadmium nitrate show no tendency to combine. C. H. B.

Basic Nitrates. By G. Rousseau and G. Tite (*Compt. rend.*, **114**, 1184—1186).—The hydrated nitrates were heated in sealed tubes between 100° and 350° in presence of fragments of marble, or, in the case of calcium nitrate, quick lime.

Nickel nitrate, at 350°, yields the salt $5NiO,N_2O_5,4H_2O$ in beautiful, green crystals that act on polarised light, and are not decomposed by boiling water.

Zinc nitrate yields the salt $5ZnO,N_2O_5,6H_2O$ in acicular crystals, which show longitudinal extinction in parallel light. The basic salt is slowly decomposed by cold water and rapidly by hot water, with formation of zinc hydroxide. This decomposition seems to have been unnoticed before, and it is probable that many of the basic nitrates described are mixtures of the hydroxide and this crystallisable basic salt.

Cadmium nitrate, between 300° and 350°, yields nacreous, white lamellæ of the composition $5CdO,2N_2O_5,8H_2O$. They show longitudinal extinction in parallel light, and are immediately decomposed by cold water with separation of amorphous cadmium hydroxide.

Calcium nitrate, in presence of the oxide at 180—200°, yields a basic salt, $2CaO,N_2O_5,2H_2O$, in needles which show longitudinal extinction. They are insoluble in alcohol, but are rapidly decomposed by water. C. H. B.

Compounds of Cuprous Iodide and Ammonium Thiosulphate. By E. Brun (*Compt. rend.*, **114**, 667—668).—When powdered cuprous iodide, or a solution of it in ammonium iodide, is added to a large excess of 50 per cent. ammonium thiosulphate solution, it

at first dissolves, but the solution soon becomes cloudy, and a well-crystallised white powder is thrown down. When this is dried by means of the filter-pump and recrystallised, it forms white crystals, having the composition $Cu_2I_2,2NH_4I,8(NH_4)_2S_2O_3$, stable at the ordinary temperature, decomposing slowly at 100°, and at a higher temperature giving off vapours of sulphur, iodine, ammonia, and sulphurous anhydride. Its solution decolorises iodine with precipitation of cuprous iodide, and is decomposed when boiled, cuprous sulphide being precipitated.

By adding a solution of cuprous iodide in ammonium iodide to one of the previous compounds, or to a more dilute solution of ammonium thiosulphate, until a slight permanent precipitate appears, a precipitate of pale yellow, crystalline needles is thrown down, having the composition $7(NH_4)_2S_2O_3,Cu_2S_2O_3,4Cu_2I_2,4H_2O$. It is insoluble in water, very unstable, and yields the same products of decomposition as the first compound.

Finally, when a concentrated solution of ammonium thiosulphate is slowly added to one of ammonium iodide saturated with cuprous iodide, taking care to avoid excess of thiosulphate, a third colourless substance is obtained, which crystallises in needles, is insoluble in water, and has the composition $Cu_2I_2,(NH_4)_2S_2O_3,H_2O$.

Potassium and sodium thiosulphates, and other iodides, such as those of silver and lead, form analogous products. Jn. W.

Graphical Chemistry of Glass. By E. Nickel (*Zeit. physikal. Chem.*, **9**, 709—721).—Roughly speaking, and neglecting chance impurities, the composition of an ordinary glass may be expressed by a formula such as $m\mathrm{Na_2O} + n\mathrm{CaO} + p\mathrm{SiO_2}$, and glasses may be compared one with another by comparing the values of m, n, and p, or better still, by fixing one of the values, say that of n, as unity and then comparing the other two m/n and p/n. In cases where other metals are present, the expression is somewhat more complicated, but leaving out of account oxides such as those of iron and aluminium, may still be given in a somewhat similar manner, for instance, with $m_1\mathrm{Na_2O} + m_2\mathrm{K_2O} + n_1\mathrm{CaO} + n_2\mathrm{PbO} + n_3\mathrm{MgO} + p\mathrm{SiO_2}$, where, instead of m/n we may write $(m_1 + m_2)/(n_1 + n_2 + n_3)$, or generally $\Sigma m/\Sigma n$. A useful method of comparing different glasses with one another would now be given by plotting the values of m/n graphically against those of p/n. Better still, however, it is to regard the glass as of the composition $\mathrm{Na_{2m}Ca_nSi_pO_{(m+n+2p)}}$ and to employ the quantity $(m + n + 2p)$, the oxygen ratio, in place of p in the comparison.

The author gives the graphic representation of a large number of different glasses in accordance with the above plan, and discusses the relationships which this mode of representation renders apparent. There does not appear to be any justification for a "normal" formula for glass, such as that proposed by Beurath, $R'_2O,CaO,6SiO_2$.

H. C.

Nickel. By P. Schützenberger (*Compt. rend.*, **114**, 1149—1154).—Pure nickel sulphate, carefully crystallised from a solution containing no free acid, was heated at 440° until it ceased to lose weight. A weighed quantity of the anhydrous sulphate was then heated for

some time between dull redness and bright redness, care being taken that the flame was always an oxidising flame. The nickel oxide left was weighed; Ni = 58·57—58·72.

The nickel oxide thus obtained was reduced in hydrogen; Ni = 58·50—58·53.

When the greenish-yellow oxide formed between dull redness and bright redness is heated almost to a white heat it contracts considerably, acquires a deeper green tint, and loses 0·4 to 0·5 per cent. in weight. This loss takes place even in an atmosphere of nitrogen, and cannot be attributed to reduction, neither does it seem to be due to dissociation. If the deep green oxide is reduced in hydrogen, the results give Ni = 59·8.

Cobalt oxide shows a similar loss of weight when very strongly heated, and analysis of the product leads to Co = 60·0.

If the strongly heated nickel oxide is reduced in hydrogen, the residue retains a small quantity of oxygen, but if allowed to remain at the ordinary temperature for 24 hours and again heated in hydrogen, a small quantity of water is immediately produced. Two or three repetitions of this process are required in order to remove the whole of the oxygen. If the first quantity of reduced nickel from this oxide is treated with warm dilute sulphuric acid the unreduced oxide remains as a very finely-divided, pale yellow powder. The reduced nickel from the strongly heated oxide does not agglomerate when heated. C. H. B.

Nickel and Cobalt Fluorides. By C. Poulenc (*Compt. rend.*, **114**, 1426—1429).—When an anhydrous metallic chloride is heated to fusion with an excess of ammonium fluoride for about a quarter of an hour, a double fluoride of ammonium and the particular metal is obtained. The whole mass is soluble in water, but the ammonium chloride formed can be removed by repeated washing with boiling alcohol. The double fluoride,* MF_n, nNH_4F, is amorphous, and when heated to redness in an atmosphere of inert gas yields an amorphous anhydrous fluoride. When the latter is heated in an atmosphere of dry hydrogen fluoride, it becomes crystalline.

Nickel fluoride, NiF_2.—The double ammonium salt is a yellowish, amorphous powder, soluble in water but insoluble in alcohol. The simple amorphous fluoride is also yellow and is almost insoluble in water. When heated in hydrogen fluoride at 1200—1300°, it is converted into beautiful, green, elongated prisms, which partially volatilise, without fusion, during their production. They are almost insoluble in water, quite insoluble in alcohol and ether, and are not attacked by warm nitric, hydrochloric, or sulphuric acid; sp. gr. = 4·63. The fluoride is converted into the oxide when heated in presence of air, into the sulphide when heated with sulphur, and into metallic nickel when heated in hydrogen. Water vapour converts it into the black oxide, or at a higher temperature into the green oxide, the crystalline form of the fluoride being retained in both cases; hydrogen

* The formulæ of the double potassium fluorides given in a previous paper (this vol., p. 781) are incorrect; they should be $NiF_2,2KF$, and $CoF_2,2KF$.

sulphide, at a red heat, yields the yellow crystalline sulphide; hydrogen chloride, on heating, converts the fluoride into the chloride; fused alkaline carbonates yield nickel oxide and alkaline fluorides.

Cobalt fluoride, CoF_2, when amorphous, is a rose-coloured powder, somewhat soluble in water. When heated in hydrogen fluoride at 1200—1300°, it melts to a ruby-red, translucid mass with a distinctly crystalline fracture, but sublimes with great difficulty even at 1400°, and in this respect differs markedly from the nickel salt. The crystallised fluoride forms small, rose-coloured prisms; sp. gr. = 4·43. It is slighly soluble in water, but insoluble in alcohol or ether. Nitric, hydrochloric, and sulphuric acids attack it slowly in the cold, and more rapidly on heating, but in other respects its properties are similar to those of the nickel compound. C. H. B.

Permolybdates. By E. Péchard (*Compt. rend.*, **114**, 1358—1361). —*Sodium Permolybdate.*— Fused sodium dimolybdate is finely powdered and mixed with hydrogen peroxide solution. On gently heating, the salt dissolves readily, and, if the yellow solution is concentrated, the permolybdate, $NaMoO_4 + 3H_2O$, separates in yellow, prismatic crystals. This salt melts at 80°, gives off oxygen at about 200°, and, when strongly heated, leaves a residue of sodium dimolybdate.

Magnesium permolybdate, $Mg(MoO_4)_2 + 10H_2O$, is obtained in a similar way, and crystallises in slender needles very soluble in water.

Barium permolybdate is obtained in a similar way, or by the action of ammonium permolybdate on barium chloride. It crystallises in microscopic, yellow octahedra of the composition $Ba(MoO_4)_2 + 2H_2O$.

Permolybdates of the heavy metals are obtained by double decomposition with ammonium permolybdate. The copper salt is greenish-yellow, and has the composition $Cu(MoO_4)_2 + H_2O$; it is soluble in ammonia and in hydrochloric and nitric acids. The silver salt, $AgMoO_4$, forms yellow, microscopic octahedra. The mercurous salt is orange, and can be used in analysis for the separation of permolybdic acid from alkaline bases. C. H. B.

Complex Inorganic Acids: Phosphotungstic Acids. By F. Kehrmann and M. Freinkel (*Ber.*, **25**, 1966—1973).—When barium chloride is added to a solution of the ammonium salt of the acid $22WO_3,P_2O_5,7H_2O$ (Abstr., 1891, 1159), a double *barium ammonium salt* is obtained, and when a slight excess of silver nitrate is added to a solution of the latter, the *salt* $22WO_3,P_2O_5,4BaO,3Ag_2O + 34H_2O$ separates in lustrous prisms. The *salt* $22WO_3,P_2O_5,7K_2O + 31H_2O$ is prepared by adding an excess of potassium chloride to a solution of phosphoduodecatungstate (*loc. cit.*), suspending the washed precipitate in boiling water, and adding thereto a dilute solution of potassium carbonate until only a small portion remains undissolved; on evaporating the filtrate, the salt separates in colourless, translucent pyramids. It is readily soluble in hot and cold water, but insoluble in alcohol, and crystalline double salts are obtained when salts of the

heavy metals are added to its concentrated aqueous solution. Thus, the salt $22WO_3,P_2O_5,2K_2O,5BaO + 48H_2O$ separates in colourless octahedra on the addition of barium chloride.

When the salt $22WO_3,P_2O_5,7K_2O + 31H_2O$, is dissolved in a little water, and, after adding an excess of dilute hydrochloric acid, the solution is boiled and filtered from potassium phosphoduodecatungstate, a potassium salt separates slowly from the filtrate; this is converted into the ammonium salt, the latter mixed into a paste with concentrated hydrochloric acid (3 parts) and nitric acid (1 part), and the mixture heated to boiling, when the salt decomposes with the evolution of nitrogen, a solution being thus obtained from which the acid $21WO_3,P_2O_5,3H_2O + 30Aq$ separates on cooling. The potassium and ammonium salts are described. The authors have studied the decomposition of the salt $22WO_3,P_2O_5,7K_2O + 31H_2O$ quantitatively, but reserve the discussion of their results until more exact data are obtained. A. R. L.

Mineralogical Chemistry.

Fluorine in Recent and Fossil Bones. By A. Carnot (*Compt. rend.*, **114**, 1189—1192).—Analyses of many human and animal bones show that the proportion of calcium fluoride varies from 0·35 to 0·63, and that of calcium chloride from 0·20 to 0·39. Elephants' tusks contain an unusually small proportion of calcium fluoride and an abnormally large proportion of magnesium phosphate.

Fossil bones from post-tertiary formations contained from 0·88 to 3·82 per cent. of calcium fluoride, the proportion of calcium chloride being practically the same as in recent bones.

Fossil bones from formations of various ages were found to contain more than 10 times as much fluorine as recent bones, the proportion of calcium fluoride reaching to as high as 6·21 per cent. This increase is doubtless due to metamorphism, the fluorine being derived either from solutions of alkaline fluorides or from slow replacement by fluorine minerals with which the bones have been in contact. Direct experiment shows that solutions of alkaline fluorides act on bones with formation of calcium fluoride. There seems to be a tendency towards the formation of a crystalline fluorophosphate containing the same proportion of fluorine as apatite, but the proportion may rise higher than in apatite by reason of the action of the alkaline fluoride on the calcium carbonate in the bone. C. H. B.

Artificial Reproduction of Leucite. By A. Dubois (*Compt. rend.*, **114**, 1361—1363).—Potassium hydrogen fluoride is slowly heated to distinct redness and alumina is added to the fused salt. Silica is then thrown in in successive small quantities until all the alumina has been dissolved. When the mass is cooled and treated

with water, crystals of leucite are obtained several millimetres in length.

Leucite is also obtained in large crystals by adding alumina to fused potassium silicofluoride, but a double fluoride of aluminium and potassium is formed at the same time, and must be removed by treatment with potassium hydroxide solution.

A third method for the preparation of leucite consists in adding silica to a fused mixture of potassium fluoride and aluminium fluoride, prepared either by heating together calcined alumina and potassium hydrogen fluoride, at first slowly and afterwards at a red heat, or by adding to fused potassium fluoride either the product of precipitating the wash waters of the previous methods by alum or the double fluoride of potassium and aluminium.

Aluminium potassium fluoride, $3KF,AlF_3$, is obtained in elongated, birefractive crystals by heating an intimate mixture of calcined alumina and potassium hydrogen fluoride, at first slowly and afterwards to complete fusion, and extracting the cooled product with water. It is only slightly soluble in boiling water, but dissolves in a moderately concentrated and warm potassium hydroxide solution.

C. H. B.

Preservation of Mineral Waters. By P. Parmentier (*Compt. rend.*, **114**, 1363—1366).—Mineral waters containing carbonic anhydride, especially if they contain iron salts also, can only be preserved unchanged by collecting them in vessels previously filled with pure carbonic anhydride. It is essential that no trace of air should remain in the collecting vessels and that the water should not come in contact with air while the vessels are being filled. C. H. B.

Organic Chemistry.

Action of Fatty Acids on Olefines. By Béhal and Desgrez (*Compt. rend.*, **114**, 676—677).—The acid residue unites with the olefine hydrocarbon having the fewest hydrogen atoms attached, whilst the acid hydrogen unites with the remaining ethylene carbon, an ethereal salt of a secondary alcohol thus being formed.

Secondary octyl acetate, $C_6H_{13}\cdot CHMe\cdot OAc$, is formed when hexyl ethylene boiling at 122°, and prepared by the action of zinc chloride on methyl hexyl carbinol, is heated with glacial acetic acid (3 vols.) in a sealed tube for 20 hours at 300°. The fraction of the product boiling above 120° is washed, dried, and redistilled, when a liquid of agreeable odour, resembling that of raspberries, passes over at 189—190°. It yields the alcohol when hydrolysed with alcoholic potash.

Secondary heptyl acetate, $C_5H_{11}\cdot CHMe\cdot OAc$, a liquid boiling at 171—173°, identical with the acetate prepared from methyl pentyl carbinol, and having a pleasant odour resembling that of myrrh,

is obtained in a similar way when the pentyl ethylene boiling at 95—96°, and prepared by heating primary heptyl iodide in a reflux apparatus with alcoholic potash, is heated with acetic acid. The heptyl iodide is conveniently prepared from the alcohol obtained by reducing œnanthaldehyde.

The diacetin of propylene glycol, $OAc{\cdot}CHMe{\cdot}CH_2{\cdot}OAc$, a liquid of agreeable odour boiling at 186—187°, is obtained when alkyl acetate is heated in a similar manner with glacial acetic acid for 25 hours at 275—285°. Jn. W.

Trimethylene. By J. W. Brühl (*Ber.*, **25**, 1952—1956).—The author's previous work has shown that in the case of compounds containing ethylene or acetylene groups, the observed molecular refractions and dispersions are greater than the calculated, whereas the values exhibit close agreement in the case of closed ring compounds containing single bonds. Thomsen found that propylene and trimethylene have the same heats of combustion. The author concludes from his determinations of the molecular refraction and dispersion of Gustavson's dichlorotrimethylene (Abstr., 1891, 159), that trimethylene is not a homologue of the olefines, and that it contains no ethylenoïd bonds. The thermic constants of the dichlorotrimethylene are being determined by Berthelot for the sake of comparing them with the isomeric propylene derivatives. A. R. L.

Higher Homologues of Acetylene. By F. Krafft and L. Reuter (*Ber.*, **25**, 2243—2251; compare Krafft, Abstr., 1884, 1108). The authors' results are in general agreement with those of Favorsky (Abstr., 1888, 798 and 1168), and they show that the hitherto known higher homologues of acetylene, from dodecylidene upwards, are di-substitution derivatives. When hexadecylene bromide, $C_{16}H_{32}Br_2$, is heated with the necessary quantity of very dilute alcoholic potash at 40—50°, *bromhexadecylene*, $C_{16}H_{31}Br$, boiling at 198—200° (18 mm.), is obtained; on heating the latter with a slight excess of alcoholic potash at 200°, methyltridecylacetylene, $CMe{:}C{\cdot}C_{13}H_{27}$, is formed; it does not give a precipitate with alcoholic silver nitrate (Béhal's reagent; Abstr., 1888, 930). When the last-mentioned hydrocarbon is heated at 200—220° with one-tenth of its weight of sodium, and the sodium derivative is decomposed by alcohol, *tetradecylacetylene*, $CH{:}C{\cdot}C_{14}H_{29}$, which gives a precipitate of the compound $C_{16}H_{29}Ag_2NO_3$ on addition of alcoholic silver nitrate, is produced; the silver derivative yields the corresponding hydrocarbon when treated with dilute hydrochloric acid in the cold. Tetradecylacetylene is also obtained when hexadecylene bromide is heated under diminished pressure with potassium hydroxide; after rectification under diminished pressure, it solidifies on cooling; it melts at 15°, boils at 155° (15 mm.), and the liquid hydrocarbon has a sp. gr. at 15° = 0·7999. On heating tetradecylacetylene with alcoholic potash at 160—180°, methyltridecylacetylene is formed. Methylpentadecylacetylene, $CMe{:}C{\cdot}C_{15}H_{31}$, boiling at 180° (15 mm.), is obtained by the action of alcoholic potash on octadecylene bromide; whereas, if the same bromide is heated with potassium hydroxide, under dimin-

ished pressure, hexadecylacetylene, $CH{:}C{\cdot}C_{16}H_{33}$, melting at 26° and boiling at 180° (15 mm.) is produced; the last-mentioned hydrocarbon has a sp. gr. in the liquid state = 0·7983 at 26°, and gives a precipitate with alcoholic silver nitrate.

Methylundecylacetylene, $CMe{:}C{\cdot}C_{11}H_{23}$, melting at 6·5° and boiling at 134° (15 mm.), and *duodecylacetylene*, $CH{:}C{\cdot}C_{12}H_{25}$, boiling at 128° (15 mm.), are obtained from tetradecylene bromide in a similar manner to the above-described homologues, and exhibit analogous behaviour to them.

Methylnonylacetylene, $CMe{:}C{\cdot}C_9H_{19}$, melting at −9° and boiling at 105° (15 mm. pressure), and *decylacetylene*, $CH{:}C{\cdot}C_{10}H_{21}$, boiling at 95—97°, have also properties analogous to their homologues.

A. R. L.

Arsenic Cyanide. By E. Guenez (*Compt. rend.*, **114**, 1186—1189).—Very finely powdered arsenic is placed in a strong flask with a slight excess of dry cyanogen iodide, and about 10 parts of very carefully-dried carbon bisulphide is added. The reaction begins at the ordinary temperature, but the flask must be heated on the water-bath for some time before the change is complete. When all the arsenic has disappeared, the product is washed with carbon bisulphide until all arsenic iodide is removed, and the insoluble part is kept in sealed vessels filled with dry carbonic anhydride.

The arsenic cyanide thus obtained has the composition $AsCy_3$, and forms yellowish, microscopic crystals. It is rapidly attacked by atmospheric moisture, and is almost instantly decomposed by water with formation of arsenious and hydrocyanic acids. When heated, about one-third of the cyanogen is given off, and a residue of arsenic and paracyanogen is left. Concentrated sulphuric acid has very little action in the cold, but on heating, sulphurous anhydride and carbonic oxide are liberated and ammonium sulphate is formed. Iodine, even in the cold, forms arsenic iodide and cyanogen iodide; if heated, the change is practically instantaneous. When mixed with potassium chlorate, arsenic cyanide detonates violently if struck.

Phosphorous cyanide has been obtained by a similar reaction.

C. H. B.

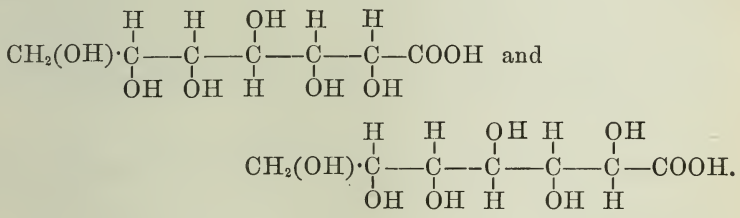
Formation of Zinc Cyanide on Heating Organic Substances containing Nitrogen with Zinc-dust. By H. Aufschläger (*Monatsh.*, **13**, 268—275).—The author finds that a very large proportion of carbon compounds containing nitrogen yield zinc cyanide when they are exposed to the action of zinc-dust at a low red heat. Such substances are the amides of carbonic acid, carbamide, and its derivatives, proteïd substances, and similarly constituted compounds; and the reaction may be conveniently employed in showing their presence. A typical reaction is that between carbamide and zinc-dust, which is represented by the equation $2CO(NH_2)_2 + 3Zn = Zn(CN)_2 + 2ZnO + 2NH_3 + H_2$, the yield of zinc cyanide being about 50 per cent. of that required by theory.

G. T. M.

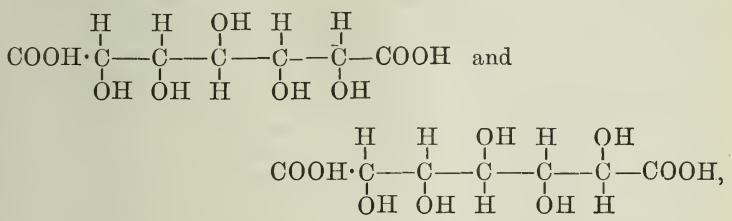
Sugars Richer in Carbon from Glucose (Dextrose). By E. Fischer and others (*Annalen*, **270**, 64—107).—In this paper experiments are described on the ascent of the glucose (dextrose) series of

sugars, the method employed being the same as used by Fischer and Passmore (Abstr., 1890, 1230) in the ascent of the mannose series. By this method two stereoisomeric glucoheptonic acids, which are provisionally designated the α- and β-compounds, are formed from glucose, thus corresponding with the case of mannose (Abstr., 1890, 1389). One of these acids, the α-compound, is identical with that obtained by Kiliani (Abstr., 1886, 526 and 687). In simpler cases, in which optically inactive materials have been dealt with, racemic compounds have invariably been produced; that is, the two stereoisomerides have been formed in equal amount. In the present case, however, the α-compound is always obtained in the larger quantity, and when the reaction is conducted at 20—25°, the quantity of the α-compound isolated in the pure state is about 73 per cent. of the theoretical, whereas the β-compound is almost absent from the product; the latter is obtained, however, to the extent of 13 per cent. when the operation is conducted at 40°, so that the course of the reaction is doubtless a function of the temperature.

Representing glucose by the configuration given by Fischer (Abstr., 1891, 1445), the two acids derived from it would have the configurations :—



Now, of the two dicarboxylic acids (pentahydroxypimelic acids) corresponding to them,



the first is optically inactive, and, as a matter of fact, it is found that the pentahydroxpimelic lactonic acid (Abstr., 1886, 936) which Kiliani obtained from his dextrosecarboxylic acid (α-glucoheptonic acid) yields an optically inactive pentahydroxypimelic lactonic acid on oxidation, whereas that obtained from β-glucoheptonic acid is optically active. It follows, therefore, that α- and β-glucoheptonic acids are represented by the configurations I and II respectively. α- and β-glucoheptose must be represented by corresponding formulæ; the synthesis having been carried further from the α-com-

pound, it is found that, as indicated by theory, two gluco-octonic acids are obtained from it; the configuration of these cannot be determined from the optical behaviour of the corresponding dicarboxylic acids, as both these are optically inactive, and, according to theory, the next possible optically active dicarboxylic acid would be derived from gluco-deconic acid, $C_{10}H_{20}O_9$.

Preparation of the Glucoheptonic Acids.—Anhydrous American grape sugar (5 kilos.) is dissolved in a large glass flask in 3 per cent. hydrogen cyanide solution (25 litres) and ordinary ammonia solution (10 c.c.) added. The mixture, after remaining at a temperature of 25° for six days, is boiled with a solution of barium hydroxide (6·7 kilos.) in water (20 litres), for several hours, until it no longer smells of ammonia; the hot filtrate is then acidified with sulphuric acid, the boiling repeated to remove the unaltered hydrogen cyanide, the sulphuric acid exactly precipitated with barium hydroxide, and the filtrate evaporated to a thick syrup in a flat dish heated by means of steam at a low tension. After remaining in the cold for several weeks, the greater portion of the α-heptonic lactone has separated; the mass is triturated with 80 per cent. alcohol, and the crystals (weighing about one-third that of the glucose employed) collected, a further quantity being obtained from the filtrate; whilst the last mother liquor yields the β-heptonic lactone (see below). The crude α-heptonic lactone is purified by dissolving it in water, and precipitating by means of alcohol, the yield of the pure compound being 30—35 per cent. of the glucose employed.

α-Glucoheptose, $CH_2(OH)\cdot\overset{H}{\underset{OH}{C}}—\overset{H}{\underset{OH}{C}}—\overset{OH}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—\overset{H}{\underset{OH}{C}}\cdot CHO$, is obtained when α-glucoheptonic lactone (50 grams) is dissolved in water (500 grams) and the solution cooled to its freezing point; dilute sulphuric acid (4 c.c.) and $2\frac{1}{2}$ per cent. sodium amalgam (250 grams) are now added with agitation, and, after a while, another small quantity of acid, so that the solution remains acid. The liquid is then again cooled to incipient freezing, and another 250 grams of sodium amalgam added as before. The operation is stopped when 750 grams of sodium amalgam have been added; it lasts about 50 minutes. Sodium hydroxide is now added to the solution until it still remains alkaline at the end of half an hour, when it is exactly neutralised with sulphuric acid, warmed with animal charcoal, the hot filtrate mixed with eight times its volume of 96 per cent. alcohol, allowed to remain at the temperature of the room for 12 hours, and then filtered from the greater portion of sodium sulphate and organic sodium salt. The alcohol is then distilled from the filtrate, and the residual solution concentrated on the water-bath to its point of crystallisation. The crystals are collected after some hours, and washed successively with 50 per cent., 80 per cent., and absolute alcohol; the dried product is then colourless, free from ash, and almost chemically pure, its amount being 32—38 per cent. of the weight of lactone employed. A considerable portion of the lactone is converted into the acid during the reaction, and may be recovered as sodium salt from the

alcoholic precipitate mentioned above. α-Glucoheptose separates from its aqueous solutions in rhombic crystals

$$a : b : c = 0{\cdot}8040 : 1 : 1{\cdot}7821,$$

which undergo no alteration at 100°; it melts at 180—190°, has a faintly sweet taste, and requires 10·5 parts of water at 14° for dissolution, being very readily soluble in hot water, and sparingly so in absolute alcohol. It exhibits birotation to a slight extent. 2·5 grams dissolved in 20 c.c. of warm water, cooled, and made up to 25 c.c. at 20°, gave the specific rotatory power $[\alpha]_{D20^\circ} = -19{\cdot}7$, and this was unaltered after 12 hours, whereas a portion dissolved in water at 20° gave, 15 minutes after preparation, $[\alpha]_{D20^\circ} = -25$; this value was reduced to the first, however, after some hours. The sugar is not fermentable with yeast, and reduces Fehling's solution somewhat less than glucose; a small quantity of furfuraldehyde is produced on heating it with dilute sulphuric or hydrochloric acid, but the chief product is humous substance. When a solution of α-glucoheptose in water (5 parts) is treated at 20° with bromine (2 parts), and at the end of three days the excess of bromine boiled off, and the hydrogen bromide precipitated with silver oxide, α-glucoheptonic acid may be isolated, the yield being 60 per cent. of the sugar.

α-Glucoheptose phenylhydrazone, $C_7H_{14}O_6{:}N_2HPh$, is very readily soluble in water, and concentrated solutions must therefore be employed in its preparation; it resembles the hydrazones of the sugars already described, melts, when quickly heated, at 170° with decomposition, and is sparingly soluble in cold alcohol, and almost insoluble in ether. The *osazone*, $C_7H_{12}O_5(N_2HPh)_2$, is prepared by heating a solution of the sugar in water (10 parts) with phenylhydrazine (2 parts) and 50 per cent. acetic acid (1 part) on the water-bath for an hour, and isolating in the usual way. It forms yellow bunches of needles, and when quickly heated darkens at 190°, and melts at 195° with evolution of gas; it requires about 60 parts of boiling absolute alcohol for dissolution, and is almost insoluble in water and ether. It closely resembles glucosazone and yields a heptosone when treated with concentrated hydrochloric acid in the manner described under oxyglucose (glucosone) (Abstr., 1888, 1267; 1889, 484). When α-glucoheptose is treated in the manner described by Erwig and Königs for the preparation of pentacetyldextrose (Abstr., 1889, 952), it yields a *hexacetyl* derivative melting at 156°, and sparingly soluble in cold water; whilst, if the sugar is heated with an equal quantity of anhydrous sodium acetate and acetic anhydride (4 parts), in a reflux apparatus for 15 minutes, *decacetyldiglucoheptose*, $C_{34}H_{46}O_{23}$, is produced; after five recrystallisations from hot water, it melts at 131—132°.

α-Glucoheptitol, $C_7H_{16}O_7$, is obtained when α-glucoheptose (10 grams) is dissolved in water (100 grams) and treated with 20 per cent. sodium amalgam (500 grams in all); the solution is kept acid, and is well agitated during the addition of the amalgam, the reaction being complete in 2—3 hours, when it no longer reduces Fehling's solution. The compound is isolated in the usual manner, and purified by repeated recrystallisation from boiling methyl or ethyl alcohol.

It crystallises in delicate prisms, melts at 127—128°, is optically inactive, and readily soluble in water, but only sparingly in alcohol. The *heptacetyl* derivative, $C_7H_9(OAc)_7$, is prepared by boiling it in a reflux apparatus for an hour with acetic anhydride and zinc chloride. After being repeatedly recrystallised from water, it forms microscopic plates, and melts at 113—115°. *Benzalglucoheptitol*, $C_7H_{14}O_7{:}CHPh$, is formed when glucoheptitol (1 gram) is dissolved in 50 per cent. sulphuric acid (1·5 c.c.) and benzaldehyde (2 grams) added with vigorous shaking; it is heated for some minutes on the water-bath, and, after 24 hours, the compound is collected, washed with water, and later with ether. It is sparingly soluble in alcohol, crystallises therefrom in delicate, felted needles, and melts at 214°. It is noteworthy that mannitol forms a tribenzyl derivative (Abstr., 1888, 950), and sorbitol and perseïtol dibenzal derivatives (*Ann. Chim. Phys.* [6], **19**, 5), under the same circumstances.

β-Glucoheptonic acid, $CH_2(OH)\cdot\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}\cdot COOH$, isolated from the last mother liquor, is obtained in the preparation of the α-acid (see above) as follows:—The syrup is boiled with an equal weight of brucine dissolved in hot water (15 parts), the solution treated with animal charcoal, and the filtrate evaporated to a syrup, the acid being in slight excess. The brucine salt separates after several hours; it is collected, washed with a little cold water, and finally recrystallised from alcohol, when it melts at 126°. To obtain the acid, the salt is dissolved in water and boiled with a slight excess of barium hydroxide; the precipitated brucine is filtered from the cool solution, the filtrate evaporated to a syrup, and triturated with cold alcohol. The barium salt is collected, dissolved in hot water, and the barium exactly precipitated with sulphuric acid; on evaporating the filtrate, the lactone principally separates, and is purified by crystallisation from hot absolute alcohol; it forms colourless delicate needles, melts at 151—152°, reduces Fehling's solution, and is very soluble in water. The values for specific rotatory power $[\alpha]_{D20°} = -67{\cdot}7$ and $-68{\cdot}6$ were found; birotation was not observed. The *calcium*, *barium*, and *cadmium* salts are all very soluble in water; the *phenylhydrazide*, $C_7H_{13}O_7(N_2H_2Ph)$, crystallises from alcohol in yellowish leaflets, and melts at 150—152°. When β-glucoheptonic lactone (4 grams) is heated with pyridine (4 grams) and water (20 grams) in a sealed tube for three hours, it is converted into α-glucoheptonic acid, which can be isolated and identified by means of its hydrazide.

β-Glucoheptose, $CH_2(OH)\cdot\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}\cdot CHO$, is prepared by reducing the corresponding lactone in 10 per cent. aqueous solution with 2½ per cent. sodium amalgam (12 parts). It has not as yet been obtained in the crystalline condition. The *phenylhydrazone*, $C_7H_{14}O_6N_2HPh$, separates on mixing the syrupy sugar (2 parts) with phenylhydrazine (1·5 parts); it crystallises from alcohol in slender,

colourless needles, darkens when rapidly heated at 190°, and melts at 192° with the evolution of gas. The osazone exhibits the same form and solubility as that prepared from α-glucoheptose, a result which was to be expected. When β-glucoheptonic lactone is oxidised with nitric acid according to Kiliani's directions (Abstr., 1886, 936), the

pentahydroxypimelic acid, $COOH\cdot\overset{OH}{\underset{OH}{C}}-\overset{OH}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot COOH$, is obtained; it is isolated by means of its *calcium* salt, from which, on decomposition with the calculated quantity of oxalic acid, evaporation, and final recrystallisation from ethyl acetate, the *lactonic* acid, $C_7H_{10}O_8$, is prepared. When repeatedly recrystallised, the latter is obtained in long needles or prisms, melts at 177°, and has the specific rotatory power $[\alpha]_{D20°} = 68{\cdot}5$. The pentahydroxypimelic acid,

$COOH\cdot\overset{OH}{\underset{OH}{C}}-\overset{OH}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot COOH$, derived from α-glucoheptonic acid,

has been described by Kiliani (*loc. cit.*); it is, as might be anticipated, optically inactive; the *phenylhydrazide* melts at 200° with decomposition, and is sparingly soluble both in alcohol and water.

Gluco-octonic Acids.—As already mentioned, two stereoisomeric octonic acids are produced by treating α-glucoheptose with hydrocyanic acid. The α-acid is always the chief product, and the amount of the β-acid formed varies with the temperature. For the preparation of the α-acid, glucoheptose (50 grams) is dissolved in water (350 grams) and anhydrous hydrogen cyanide (14 c.c.) added, the mixture being contained in a well-closed flask, and kept in an incubator at 25° for four days, after which it is boiled with barium hydroxide (50 grams) until the ammonia is expelled, diluted to redissolve the basic salt thus formed, and then treated with carbonic anhydride until neutral; the filtrate is evaporated, and the barium salt of the α-acid collected, that of the β-acid remaining in the mother liquor. α-Gluco-octonic acid is prepared from the barium salt in the usual manner; it yields the *lactone*, $C_8H_{14}O_8$, on evaporating its aqueous solution. The latter is very sparingly soluble in ethyl alcohol, somewhat more so in methyl alcohol, and very readily in water; it melts at 145—147°, and has a specific rotatory power $[\alpha]_{D20°} = 45{\cdot}9$. The *barium*, *calcium*, and *cadmium* salts are crystalline; the *phenylhydrazide* forms slender, colourless needles, and, when rapidly heated, melts at 215°.

α-Gluco-octose, $C_8H_{16}O_8 + 2H_2O$, is obtained by reducing α-gluco-octonic lactone (50 grams) with sodium amalgam (625 grams) in the manner described for the preparation of α-glucoheptose (see above); it crystallises in delicate, colourless needles, melts at 93°, loses its water of crystallisation partially when placed over concentrated sulphuric acid, but apparently not completely when heated for 48 hours at 75° under diminished pressure; it is only sparingly soluble in hot ethyl alcohol, but more readily in methyl alcohol. It exhibits birotation; the specific rotatory power calculated on the anhydrous sugar is $[\alpha]_{D20°} -50{\cdot}5$. The *phenylhydrazone*, $C_8H_{16}O_7(N_2HPh)$, is

sparingly soluble in cold water, and melts at 190° when rapidly heated. The *phenylosazone*, $C_8H_{14}O_6(N_2HPh)_2$, is almost insoluble in water, and melts at 210—212° when rapidly heated.

α-Gluco-octitol, $C_8H_{18}O_8$, is formed by reducing the last-described sugar with sodium amalgam; it forms slender, white needles, melts at 141°, and is readily soluble in water, very sparingly in ethyl alcohol, but somewhat more so in methyl alcohol. It has a specific rotatory power in 10 per cent. solution $[\alpha]_{D20°} = 2$, and when an equal weight of borax is dissolved in the solution the specific rotatory power is trebled.

β-Gluco-octonic acid is obtained from the mother liquor, after the separation of the α-acid in the preparation of α-gluco-octonic acid, when the same is conducted at a temperature of 40°; the yield amounts to about 15 per cent. of the heptose employed. The *lactone* is sparingly soluble in alcohol, and crystallises therefrom in colourless, slender needles, or from water in large, well-formed prisms, melts at about 186—188°, and has a specific rotatory power $[\alpha]_D = 23{\cdot}6$. The *phenylhydrazide* melts at 172°.

When α-gluco-octonic lactone is heated with pyridine and water in a sealed tube at 140°, it is partially converted into the β-compound.

Glucononic Acid.—When α-gluco-octose (30 grams) is dissolved in water (150 grams), and after the addition of anhydrous hydrogen cyanide (4·8 c.c.), the mixture kept at a temperature of 10—17° for 11 days, a small quantity of a substance separates, which is, perhaps, a nononic amide; the reaction is completed by keeping the mixture in an incubator at a temperature of 25° for two additional days. Two acids, probably stereoisomerides, are formed, that which is most readily isolated only being examined. When phenylhydrazine is added to a solution of the acid obtained from the crude barium salt, and the mixture heated on the water-bath for an hour, a hydrazide separates on cooling; this is described below; whilst a more soluble hydrazide, melting at 40° lower, may be obtained from the filtrate. The *lactone* obtained by evaporating a solution of the acid, prepared from the purified barium salt, is dextrorotatory, does not reduce Fehling's solution, and is very soluble in water, but only sparingly in alcohol; the *phenylhydrazide*, $C_9H_{19}O_9,N_2H_2Ph$, melts at 234°, and is sparingly soluble in hot water.

Glucononose, $C_9H_{18}O_9$, is prepared by reducing the last-described lactone in 10 per cent. solution with sodium amalgam at 0°; it was only obtained as a syrup. The *phenylhydrazone*, $C_9H_{18}O_8{\cdot}N_2HPh$, is sparingly soluble in cold water and alcohol, and melts at 195—200°; the *phenylosazone*, $C_9H_{18}O_7(N_2HPh)_2$, is formed by heating the sugar with an excess of phenylhydrazine acetate, on the water-bath, for some hours; it is very sparingly soluble in hot water or alcohol, somewhat more readily so in dilute alcohol, and melts at 220—223°. Unlike mannononose (Abstr., 1890, 1233), glucononose does not ferment with yeast.

Glucononitol, $C_9H_{20}O_9$, is prepared by reducing crude, syrupy glucononose in the same manner as already described for the reduction of glucoheptose (see above). It is separated from sodium salts by taking advantage of its slight solubility in strong alcohol. It crys-

tallises from hot water in elongated tables or prisms, commences to sinter at 190°, and melts at 194°; it is readily soluble in hot water, very sparingly soluble in alcohol, and does not reduce Fehling's solution. A. R. L.

β-Galactan. By E. Schulze (*Ber.*, **25**, 2213—2218).—β-Galactan is a carbohydrate obtained from lupine seeds which, when boiled with dilute sulphuric acid, yields galactose. It has been described by E. Steiger (*Ber.*, **19**, 827), who, on analysing specimens dried at 115°, obtained numbers agreeing with the formula $C_6H_{10}O_5$.

The author has prepared β-galactan from lupine seeds, and confirms Steiger's results as to its properties. It yields the largest quantity of glucose when boiled for 1½ hours with one-fifth normal hydrochloric acid. The yield, however, is only 80 per cent. of that required by theory; the loss is due to some of the fruit sugar which is formed being decomposed. The product of the inversion consists of galactose, fruit sugar, and another sugar, which the author has not yet examined. Mannose and pentose could not be detected.

The author has analysed specimens of β-galactan dried at 100°, and obtained numbers agreeing with the formula $C_{12}H_{22}O_{11}$, or a multiple of the same. The specific rotation of the product, when dried at 100° in 5 per cent. aqueous solution at 22°, is $[\alpha]_D = +138°$. When dried at 110—115° $[\alpha]_D = +150°$. Three other preparations gave $[\alpha]_D =$ 148·7°, 149·8°, and 147·2°.

The author proposes to substitute the name *lupeose* for β-galactan. E. C. R.

Iodide of Starch. By G. Rouvier (*Compt. rend.*, **114**, 1366—1367).—In order to determine the composition of iodide of starch prepared in presence of excess of starch, a quantity of starch solution was mixed with a definite volume of a standard iodine solution, and a volume of a saturated solution of ammonium chloride, equal to the starch solution, was added. The precipitate was washed with ammonium chloride solution, and the carbon and iodine determined. The proportion of iodine varied from 8·57 to 9·12 per cent., whilst the proportion calculated for the formula $(C_6H_{10}O_5)_8I$ is 8·92 per cent. According to the author this result agrees with that of Mylius, who found (Abstr., 1887, 568) that the product of the action of an excess of iodine on starch is $(C_6H_{10}O_5)_4I$. C. H. B.

Product of the Oxidation of Starch. By P. Petit (*Compt. rend.*, **114**, 1375—1377).—When 4 parts of starch, containing 20 per cent. of water, is mixed with 5 parts of pure ordinary nitric acid, a gummy mass is obtained, which, when heated at 40° for several days, swells up, becomes green, and finally yields a very bulky, white, porous product, equal in weight to the original starch.

When this product, which contains 6 per cent. of nitric acid, is heated at 100°, it becomes reddish-yellow, and then gives off reddish vapours. When treated with water carbonic anhydride and nitrogen oxides are evolved, the evolution of gas being very abundant on heating, whilst dissolution is practically complete. In presence of alcohol there is less evolution of gas, and solution is much less complete in the cold;

but on heating there is a violent evolution of gas, and about half of the solid matter dissolves.

The addition of ether to a cold alcoholic solution precipitates a white, gummy substance, which gradually becomes less soluble in alcohol. When purified by solution in water, and reprecipitation by alcohol, it has the composition $C_5H_6O_5$. It dissolves very readily in water, and the acid solution is strongly dextrogyrate; it reduces ammoniacal silver nitrate and Fehling's solution in the cold. Its specific rotatory power is $\alpha_j = +152{\cdot}8$, and its reducing power is equal to 24·2 per cent. of that of glucose. The acid is monobasic with phenolphthaleïn as indicator, and with barium hydroxide gives the salt $(C_5H_5O_5)_2Ba$, but if this is left in contact with the mother liquor it partially redissolves, and about half as much more alkali is required to produce a coloration with the phenolphthaleïn.

When thrown into a concentrated solution of phenylhydrazine acetate, the acid yields a hydrazone, $C_5H_6O_4{:}N_2HPh$, crystallising from boiling water in rudimentary needles that melt with decomposition at about 100°.

The acid is insoluble in cold alcohol, but if boiled for a long time with water, or for a shorter time with dilute inorganic acids, it is converted into a new acid, $C_5H_8O_6$, which is readily soluble. The ammonium salt of the latter, $C_5H_7O_6{\cdot}NH_4$, is sometimes obtained as a deliquescent amorphous product by the action of ammonia gas on the cold alcoholic solution of the original product. The corresponding hydrazone, $C_5H_8O_5{:}N_2HPh$, forms readily at 60—70°, and in a dry vacuum it loses water and changes into the hydrazone of the acid $C_5H_6O_5$.

The acid $C_5H_8O_6$ is monobasic, and its potassium and cadmium salts are amorphous. C. H. B.

Chlorine Derivatives of Isobutylamines. By A. Berg (*Compt. rend.*, **114**, 1379—1382).—The chlorine derivatives of the isobutylamines were prepared by the method previously used for the corresponding derivatives of the amylamines, namely, the action of sodium hypochlorite on the hydrochlorides of the bases (Abstr., 1890, 952).

Monochlorisobutylamine, $NHCl{\cdot}C_4H_9$, is a colourless, oily liquid, with a very pungent odour and taste; sp. gr. at 0° = 0·986. It is only slightly stable, and changes to a crystalline mass after some hours. It is, however, more stable than the corresponding amyl compound, and can be boiled without immediate decomposition. Sulphuric acid of 25 per cent. converts it into dichlorisobutylamine and isobutylamine, whilst with hydrogen chloride, in presence of ether, it yields diisobutylamine hydrochloride, chlorine gas being evolved.

Dichlorisobutylamine, $NCl_2{\cdot}C_4H_9$, is obtained by distilling isobutylamine hydrochloride with 10 times its weight of bleaching powder. It is found in the first part of the distillate, and is treated with sodium thiosulphate solution, then with 25 per cent. sulphuric acid, and, finally, with 50 per cent. acid, in order to remove all traces of the monochloro-derivative, which would reduce its stability. Dichlorisobutylamine is a golden-yellow liquid, with a strong, irritating, chlorinous odour; it boils without decomposition at 37° under a pressure of

24 mm.; sp. gr. at 0° = 1·093. With hydrochloric acid, in presence of ether, it yields chlorine and isobutylamine hydrochloride.

Chlorodiisobutylamine, $NCl(C_4H_9)_2$, is a colourless, oily liquid, with a feeble disagreeable odour; sp. gr. at 0° = 0·891. It does not solidify at −40°; it boils at 61° without decomposition under a pressure of 19 mm., and with decomposition at about 163° under the ordinary pressure. At the ordinary temperature it slowly decomposes with deposition of crystals. Hydrochloric acid converts it into diisobutylamine hydrochloride, with liberation of chlorine.

Isobutylisobutylideneamine, $C_4H_9{\cdot}N{:}C_4H_8$, is obtained by the action of alcoholic soda on monochlorodiisobutylamine. It boils at 130—131° under a pressure of 760 mm. When distilled with excess of hydrochloric acid, it yields isobutylyamine and isobutaldehyde, and it can be formed, with development of heat and liberation of water, by mixing these two compounds in molecular proportion.

Diisobutylcyanamide, $NCy(C_4H_9)_2$, is obtained by the prolonged boiling of an alcoholic solution of chlorodiisobutylamine with a very concentrated aqueous solution of potassium cyanide. It is an oily liquid, which boils at 116—117° in a vacuum. It has a feeble aromatic odour and feeble basic properties, is insoluble in water, and dissolves in hydrochloric acid, but is precipitated from the latter on dilution. When heated with hydrochloric acid at 130°, it yields carbonic anhydride, ammonia, and diisobutylamine. C. H. B.

Hexamethyleneamine. By L. Hartung (*J. pr. Chem.* [2], **46**, 1—20).—*Hexamethylene benzochloride*, $C_6H_{12}N_4ClBz$, is a white, amorphous substance, which separates from a hot solution of hexamethyleneamine in benzene on the addition of an excess of benzoic chloride; it decomposes at 60°, is somewhat soluble in hot alcohol, insoluble in ether and benzene, and partially soluble in water, with separation of benzoic acid. The precipitate obtained by substituting acetic chloride for benzoic chloride was not analysed.

When hexamethyleneamine is heated with an excess of ethyl chloracetate at 110°, 2 mols. of it react with 1 of the chloracetate with elimination of alcohol and formation of the *compound* $C_{14}H_{25}ClN_8O$. This is white, decomposes at 50°, is easily soluble in water and alcohol, but insoluble in ether and benzene; the *platinochloride*, $C_{14}H_{25}ClN_8O,HCl,PtCl_4 + H_2O$, is an amorphous, red precipitate. The *hydrochloride* forms aggregates of needles, and is obtained when hexamethyleneamine is heated with an excess of ethyl chloracetate in absolute alcohol in a reflux apparatus.

In studying the action of sulphurous anhydride on hexamethyleneamine, it was found that when the gas is passed through a hot solution of the base in alcohol, isobutyl alcohol, or isopropyl alcohol, a white *compound*, $C_5H_{11}N_3SO_3$, is obtained; this is freely soluble in water but insoluble in the usual organic solvents; when titrated with decinormal iodine solution, only half of its sulphur is completely oxidised thereby; when it is oxidised by potassium permanganate, aldehyde is evolved. Another *compound*, $C_6H_{22}N_4S_2O_{10}$, is formed when methyl alcohol is the solvent; this is reddish in colour but possesses properties similar to those of the white compound; only

half of its sulphur is oxidised by iodine. When benzene is the solvent, a molecular *compound* of the hexamethyleneamine and sulphurous anhydride, of the formula $C_6H_{12}N_4,SO_2$, is produced; it is colourless and crystalline, dissolves easily in water, but only sparingly in alcohol, and decomposes at 60°.

Methylamine is the most noticeable and constant product of the action of acids on hexamethyleneamine. Ammonia and methyleneaniline are produced when hexamethyleneamine and aniline are heated together. A. G. B.

Configuration of Aldoximes. By W. Dollfus (*Ber.*, **25**, 1908—1926).—The author's experiments show that aliphatic aldoximes are only stable in one form, for, whilst they can be converted into hydrochlorides in a manner similar to the aromatic aldoximes when treated with hydrogen chloride in ethereal solution, these, on decomposition with alkali, give the original aldoxime. Lach has shown (Abstr., 1884, 1154) that when certain aliphatic aldoximes are heated with acetic anhydride, nitriles are formed. The author finds that when acetaldoxime is mixed with a slight excess of acetic anhydride with cooling, the mixture placed aside for a day, and carefully neutralised with potash, ether extracts acetonitrile; propionaldoxime, isobutyraldoxime, isovaleraldoxime, and œnanthaldoxime are converted into nitriles in the same way. The reaction proceeds quantitatively in each case, and it would seem to be the best method of converting aldehydes into nitriles. It shows, moreover, that these aldoximes may be represented by the general configuration $\begin{matrix}R\cdot C\cdot H\\ \|\\ N\cdot OH\end{matrix}$ (synaldoximes, see this vol., p. 312). The same applies to the aldoximes mentioned below. Phenylacetaldehyde is obtained according to Cannizzaro's directions (*Annalen*, **119**, 223) by distilling calcium phenylacetate; when regenerated from its hydrogen sulphite compound, it is fractionated and passes over at 193—195°. The *oxime*, $CH_2Ph\cdot CH{:}NOH$, melts at 97—99°, and when treated with acetic anhydride as above described, yields an oil, from which, after boiling with soda and acidifying, phenylacetic acid is obtained by extraction with ether. Hydrocinnamaldoxime (b. p. 208°), when treated with acetic anhydride, gives hydrocinnamonitrile; cinnamaldoxime gives the *acetyl* derivative, $CHPh{:}CH\cdot CH{:}NOAc$, melting at 69—70°, which, however, readily decomposes into cinnamonitrile and acetic acid on treatment with water; whilst when crotonaldoxime is dissolved in ether (10 parts) and an excess of acetic anhydride added, crotononitrile is formed (compare Schindler, this vol., p. 580).

Ortho-substituted aromatic aldoximes appear, in accordance with the observations of others, to be only capable of existence in one modification, which must, however, be represented by the anti-configuration, $\begin{matrix}R\cdot C\cdot H\\ \|\\ OH\cdot N\end{matrix}$ (*loc. cit.*), since they yield, on treatment with acetic anhydride, acetyl derivatives which give the original oxime but no nitrile on decomposition with water or alkali; the cases examined by the author are orthomethylbenzaldoxime, orthochloro-

benzaldoxime, and orthomethoxybenzaldoxime; the same is true of metahydroxybenzaldoxime, and of the corresponding parahydroxy-derivative, although parachloro-, nitro-, and methoxy-benzaldoxime are each known to exist in two modifications. A. R. L.

Relations between Constitution, Configuration, and Chemical Behaviour of Oximes. By A. Hantzsch (*Ber.*, **25**, 2164—2185).—A theoretical paper dealing with the subject from the point of view of the well-known theory of Hantzsch and Werner. The facts cited have all appeared in this journal. The matter is discussed under two headings, viz.:—I. *Influence of the constitution of asymmetrical oximes on the stability or existence of the two configurations* $\begin{matrix}X\cdot C\cdot Y\\ \|\\ HON\end{matrix}$ and $\begin{matrix}X\cdot C\cdot Y\\ \|\\ NOH\end{matrix}$. II. *Influence of configuration (and consequently of constitution) on the intramolecular reactions of asymmetrical oximes.*

A. R. L.

Stereoisomeric Dioximes from Ethyl Acetoacetate and Benzoylacetate. By G. Nussberger (*Ber.*, **25**, 2142—2164).—This investigation was undertaken in view of the fact that stereoisomerism has only heretofore been observed in mono- and di-carboxy-derivatives of aliphatic dioximes.

The two compounds described by Cérésole and Köckert (Abstr., 1884, 1120) as ethyl $\alpha\beta$-diisonitrosobutyrate and its anhydride are now shown to be *ethyl methylsynglyoximecarboxylate*,

$$\begin{matrix}Me\cdot C\text{———}C\cdot COOEt\\ \|\quad\quad\quad\|\\ N\cdot OH\quad HO\cdot N\end{matrix},$$

and *hydroximidomethylsynoxazolone*, $\begin{matrix}Me\cdot C\cdot C(NOH)\cdot CO,*\\ \|\quad\quad\quad\quad\quad|\\ N\text{———}O\end{matrix}$ respectively, and are thus obtained:—

Crude, oily ethyl hydroximidoacetoacetate prepared by the action of nitrous acid at 0° on ethyl acetoacetate is treated with somewhat more than the molecular proportion of hydroxylamine hydrochloride in dilute alcoholic solution. The product is extracted with ether, and the ethereal solution shaken with soda solution, which extracts the above-mentioned oxazolone, whilst ethyl methylsynglyoximecarboxylate remains dissolved. Ethyl methylsynglyoximecarboxylate crystallises from ether in white, concentrically-grouped needles, darkens at 115°, and melts at 142° with evolution of gas; it is soluble in alcohol, ether, and hot water, and dissolves in alkalis forming a colourless solution, from which it is precipitated unchanged on acidification, but is absolutely insoluble in acids; a green precipitate is produced on adding copper sulphate to its neutral solution.

The diacetyl derivative, $\begin{matrix}Me\cdot C\text{———}C\cdot COOEt\\ \|\quad\quad\quad\|\\ N\cdot OAc\quad AcO\cdot N\end{matrix}$, is obtained by

* That this compound has not the alternative formula $\begin{matrix}CMe\cdot C\cdot COOH\\ \|\quad\quad\|\\ N\cdot O\cdot N\end{matrix}$ is shown by its bad electrical conductivity, and its very small dissociation constant.

dissolving the oxime in acetic anhydride and allowing the solution to evaporate over sulphuric acid and soda in a vacuum; it crystallises in white needles, melts at 50°, is readily soluble in ether, less so in alcohol and chloroform, and almost insoluble in cold water, but can be crystallised from hot water without decomposition; it dissolves in alkalis without coloration, and ethyl methylsynglyoximecarboxylate separates on adding an acid; if, however, the alkaline solution has been kept a long time, the corresponding acid (see below) is obtained on acidification, whilst, if the same solution is boiled, it becomes red after a while, and on the addition of acid yields hydroximidomethylsynoxazolone.

Methylsynglyoximecarboxylic acid, $\begin{matrix}\mathrm{Me\cdot C}\text{———}\mathrm{C\cdot COOH}\\ \mathrm{N\cdot OH\ \ HO\cdot N}\end{matrix}$, is formed when the ethyl salt is allowed to remain for a day with an excess of concentrated sodium hydroxide solution, the unchanged ethyl salt extracted with ether, and after cautiously acidifying the solution, extracting the acid with ether. On crystallisation from ether, it is obtained in white cubes containing 2 mols. H_2O; it loses $1\frac{1}{2}$ mols. H_2O in the desiccator, but the remaining $\frac{1}{2}$ mol. is not removed below the temperature at which it undergoes decomposition. It is readily soluble in water, alcohol, and ether, sparingly so in chloroform, and insoluble in light petroleum, and melts at 120—121°; it dissolves in alkalis without coloration, and is precipitated unchanged by acids; in aqueous or neutral solution it gives, with silver and mercurous nitrates, white precipitates, and with copper acetate a yellowish-brown precipitate, with ferric chloride a brown coloration, but with lead acetate neither precipitate nor coloration.

Ethyl methylamphiglyoximecarboxylate, $\begin{matrix}\mathrm{Me\cdot C}\text{——}\mathrm{C\cdot COOEt}\\ \mathrm{N\cdot OH\ \ N\cdot OH}\end{matrix}$, is obtained by passing dry hydrogen chloride through an ethereal solution of the syn-compound; it crystallises in white, ramified needles, melts at 132°, and is readily soluble in ether, alcohol, and chloroform, but insoluble in water, and gives neither a precipitate nor a coloration with copper acetate. The compound dissolves in alkali carbonates, and is precipitated unchanged on acidification, but if it is dissolved in alkali hydroxides, ethyl methylsyngloximecarboxylate separates on the addition of acid; the protracted action of alkali hydroxides, however, gives rise to the acid corresponding with the last-named salt.

The *diacetyl* derivative, $\begin{matrix}\mathrm{Me\cdot C}\text{———}\mathrm{C\cdot COOEt}\\ \mathrm{N\cdot OAc\ \ N\cdot OAc}\end{matrix}$, is prepared from the last-described compound by the method given above for the preparation of the stereoisomeride; it is also formed when ethyl methylsynglyoximecarboxylate is treated in ethereal solution with acetic chloride. It is a micro-crystalline powder, melts at 119—120°, is readily soluble in ether and alcohol, sparingly so in cold water, and is converted into ethyl methylamphiglyoximecarboxylate when boiled with water. The diacetyl derivative, moreover, dissolves in alkalis with a reddish colour, from which acids precipitate ethyl methylsynglyoximecarboxylate.

Hydroximidosynoxazolone (see above) is obtained when methylsynglyoximecarboxylic acid is treated at the ordinary temperature with hydrogen chloride, mere exposure of the latter to the acid vapours of the laboratory being sufficient to bring about the change; it crystallises in leaflets of the formula $C_4H_4N_2O_3 + \frac{1}{2}H_2O$, loses its water of crystallisation at 100°, melts at 132°, and is readily soluble in water, alcohol, and ether, very sparingly so in benzene. Its aqueous solutions have an acid reaction, and it forms salts with alkalis and ammonia, the solutions of which are red; the neutral solution of the ammonium salt gives, with copper acetate, a brown, and with lead acetate a red, coloration, with silver nitrate a brick-red precipitate, but no alteration with either mercuric nitrate or ferric chloride. Acetic anhydride, at the ordinary temperature, acetic chloride, and hydrochloric acid have no action on it. Hydroximidosynoxazolone may be regarded as the inner anhydride of methylamphiglyoximecarboxylic acid, $\begin{matrix}Me\cdot C & \text{——} & C\cdot COOH\\ \| & & \|\\ N\cdot OH & & N\cdot OH\end{matrix}$, which cannot be isolated in the free state; for example:—When the first-named compound is treated with an excess of alkali, the red colour at first formed quickly vanishes, and the neutralised solution gives, with mercurous nitrate, a white precipitate, and with ferric chloride a brown coloration; also a dark green coloration with copper acetate, a yellow precipitate with silver nitrate, and a white precipitate with lead acetate. As these reactions taken together differ from those exhibited by solutions of either the syn-acid or hydroximidosynoxazolone, they may be taken as indicative of the presence of the amphi-acid. When, however, the above-mentioned, colourless, alkaline solution is ever so carefully neutralised, under all circumstances, hydroximidosynoxazolone is obtained on extraction with ether.

When methylsyngloximecarboxylic acid is dissolved in acetic anhydride, a white, monacetyl derivative is formed; this dissolves in alkalis with a rose colour, undergoing hydrolysis, and melts at 150°; its configuration and constitution were not determined.

Hydroximidophenylsynoxazolone, $\begin{matrix}Ph\cdot C & \cdot C(NOH)\cdot CO\\ \| & \quad\quad\quad |\\ N & \text{————} \quad O\end{matrix}$, has been prepared by Claisen and Zedel (Abstr., 1891, 468) and by Hantzsch (*ibid.*, 740), and described in each case as phenylisoxazolone.

Phenylamphiglyoximecarboxylic acid, $\begin{matrix}Ph\cdot C & \text{——} & C\cdot COOH\\ \| & & \|\\ N\cdot OH & & N\cdot OH\end{matrix}$ (?), is a labile compound, but the existence of its salts is indicated as follows:—When hydroximidophenylsynoxazolone is dissolved in an excess of aqueous sodium hydroxide and the solution allowed to remain and carefully neutralised, a colourless solution is obtained, that of the oxazolone salt being red; this solution gives, with copper acetate, a blackish-brown coloration, with lead acetate a white precipitate, and undergoes no alteration on addition of mercuric chloride. On acidification and extraction with ether, the acid is obtained, but soon undergoes conversion into hydroximidophenylsynoxazolone.

Phenylsynglyoximecarboxylic acid, $\begin{matrix}Ph\cdot C & \text{————} & C\cdot COOH\\ \| & & \|\\ N\cdot OH & & HO\cdot N\end{matrix}$ (?).—

The following evidence of the existence of this acid was obtained:—When hydroximidophenylsynoxazolone is dissolved in boiling aqueous sodium carbonate, the solution, on neutralisation, gives, with lead acetate, a white precipitate, with copper acetate a bright green coloration, and with mercuric chloride neither precipitate nor coloration. On acidifying the solution and extracting it with ether, *phenylazoxazolecarboxylic acid*, $\begin{matrix} C\cdot Ph\cdot C\cdot COOH \\ \| \quad\quad \| \\ N\text{–}O\text{–}N \end{matrix}$, is isolated. It crystallises in white, rhombic tables, melts at 110°, and is readily soluble in water, alcohol, and ether, but almost insoluble in benzene. It has all the properties of a carboxylic acid, forms colourless salts, gives no noticeable reactions with copper and lead acetates, but with silver nitrate and mercuric chloride, white precipitates; the *methyl* salt melts at 35°. A. R. L.

Action of Magnesium Acetate on Magnesium Oxide and on Lead Oxide. By Kubel (*Arch. Pharm.*, **230**, 173—182).—More than one deodoriser consists of a mixture of magnesium acetate solution with magnesium oxide, but the quantity of the oxide which actually dissolves in the solution is very small, and whether a basic magnesium acetate is formed is undecided. Lead oxide readily dissolves in a solution of magnesium acetate, tribasic lead acetate, $2PbO,Pb(C_2H_3O_2)_2$, being thereby formed. The solution is readily precipitated by carbonic anhydride, with the production of white lead. Silver nitrate gives a yellow precipitate with the solution; potassium iodide gives a white precipitate, which becomes yellow after a time; chlorine-water gives, after a time, a brown precipitate of lead peroxide. According to the author, ordinary basic lead acetate solution contains only bibasic lead acetate, together with the normal salt. When a 10 per cent. solution of magnesium acetate is boiled with 7 per cent. of lead oxide, and set aside for some hours until the excess of tribasic lead acetate has separated, the liquid still contains 4 per cent. of lead oxide; this forms a ready method of preparing a solution of such strength. A. G. B.

Constitution of Ethyl Sodacetoacetate. By A. Michael (*J. pr. Chem.* [2], **45**, 580—590).—Nef (this vol., p. 145) says that the action of ethyl sodacetoacetate on ethyl chlorocarbonate gives rise to the formation of ethyl acetylcarbintricarboxylate, together with ethyl acetomalonate, and regenerated ethyl acetoacetate. This reaction has already been studied by the author (Abstr., 1888, 1054), who found that the product is almost entirely ethyl carbethoxacetoacetate, only a little ethyl acetomalonate being formed at the same time. With phenylhydrazine acetate, ethyl carbethoxacetoacetate yields phenylmethylpyrazolone and a substance which melts at 80—81°; with free phenylhydrazine, no water or ethyl acetoacetate was formed, as Nef (*loc. cit.*) states to be the case with his compound, but the substance which melts at 80—81° and two oils, one acid and the other neutral, were isolated.

The action of ethyl chlorocarbonate on ethyl sodethylacetoacetate yields, as the main product, *ethyl carbethoxethylacetoacetate*,

$$COOEt{\cdot}O{\cdot}CMe{:}CEt{\cdot}COOEt;$$

this boils at 146° (20 mm.), and is converted by solid sodium ethoxide into ethyl acetoacetate, ethyl carbonate, and sodium carbonate; with phenylhydrazine it yields the substance which melts at 80—81° (see above). A *compound*, $COMe{\cdot}CEt(COOEt)_2$, isomeric with the one just described, is obtained by the action of acetic chloride on ethyl sodethylmalonate; it boils at 137° (20 mm.), and is converted by sodium ethoxide into ethyl ethylmalonate, ethyl acetate, and sodium acetate; with phenylhydrazine, it forms the compound $N_2H_2Ph{\cdot}COMe$; with phenylhydrazine acetate in dilute alcohol, the hydrazone, $N_2HPh{:}CMe{\cdot}CEt(COOEt)_2$ (m. p. 43—44°), is formed. The *methyl* derivatives, corresponding to the two above-mentioned ethyl derivatives, boil at 137° and 131—131·5° (20 mm.) respectively, and are prepared in a similar manner.

Some remarks on the formation of pyrazolones follow, involving the citation of experiments, the details of which are shortly to appear. The author points out that Nef's statements that ethyl ethylacetoacetate in ethereal solution is not reduced by sodium and that the calculated amount of hydrogen is evolved are incorrect, only some five-sevenths of the calculated hydrogen being actually obtained. Nef also states that ethyl malonate which has been dried by silicon chloride is not attacked by sodium; the fact being that both a silicon derivative and also hydrogen chloride are produced, and the latter attacks the sodium. A. G. B.

Action of Iodic Acid on Lævulinic Acid. By A. Angeli and A. Chiussi (*Ber.*, **25**, 2205—2208).—The authors have obtained an acid which they believe to be diiodacetoacrylic acid.

Diiodacetoacrylic acid, $C_5H_4I_2O_3$, is obtained by adding pure lævulinic acid (9 grams) to a boiling solution of iodic acid (7 grams) in water (30 c.c.); a vigorous reaction takes place, and, on cooling, the product separates as a bright yellow, crystalline compound. It crystallises from boiling acetic acid in large, yellow scales, decomposes at 150—160° with evolution of iodine, is insoluble in water, ether, benzene, and chloroform, easily soluble in alcohol, ethyl acetate, and acetic acid, and decomposes in solution in the light, or on heating, with evolution of iodine. When treated with an alkaline carbonate, it yields iodoform and a new acid which has not been further examined. When treated with hydriodic acid, it is decomposed and yields acetoacrylic acid, $CHAc{:}CH{\cdot}COOH$.

The *oxime* of *moniodacetoacrylic acid*, $C_5H_5IO_2{:}NOH$, is obtained when the above diiodo-acid, dissolved in alcohol, is warmed on the water-bath with twice the quantity of hydroxylamine hydrochloride. It melts at 155° with decomposition, and, by the further action of hydroxylamine, yields acetoacrylic oxime.

Acetoacrylic oxime, $C_5H_7NO_3$, is best obtained by adding the diiodo-acid to a boiling, aqueous solution of hydroxylamine hydrochloride; iodine is evolved, and, on decolorising the mixture with sulphurous acid

and extracting with ether, a solid, colourless product is obtained. It melts at 189°, with evolution of gas, has acid properties, is easily soluble in alcohol and warm water, less so in cold water, ethyl acetate, benzene, and chloroform, and reduces Fehling's solution. The *monacetate*, $C_5H_6NO_3Ac$, melts at 143°. This acetoacrylic oxime is not identical with the oxime prepared directly from acrylic acid by Wolff. The latter melts at 206°, and its acetate at 155°. The oxime melting at 189° is converted by boiling with water into the higher melting isomeride. The authors put forward the following formulæ for these two compounds :—

$$\underset{\text{OH·N}}{\overset{\text{Me·C·CH:CH·COOH}}{\|}} \quad \text{and} \quad \underset{\text{N·OH}}{\overset{\text{Me·C·CH:CH·COOH}}{\|}}$$

M. p. 189°. M. p. 206°.

E. C. R.

So-called Isoarabinic Acid. By C. Scheibler and H. Mittelmeier (*Ber.*, **25**, 1964—1966).—The authors have repeated Ballo's experiments (Abstr., 1889, 693), and arrive at the conclusion that the so-called "isoarabinic acid" there described is not a compound related to the carbohydrates. The acid, prepared according to Ballo's directions by the action of ferrous sulphate on tartaric acid, was converted into the calcium salt, and thence into the potassium salt. A determination of potassium in the latter gave K = 18·38 per cent., whereas Ballo found K = 19·15—19·5 per cent. To prepare the free acid, a solution of the potassium salt was treated with lead acetate, and the precipitate collected; the filtrate gave a further precipitate on the addition of basic lead acetate. Both precipitates were suspended in water, and decomposed by a current of hydrogen sulphide, the filtrates being concentrated, when, instead of an amorphous acid, in both cases crystalline substances separated, which proved to be tartaric acid. The authors find, moreover, that when potassium "isoarabinate" is dissolved in water, and heated on the water-bath with potassium hydroxide, ordinary potassium tartrate separates on allowing the solution to remain. Ballo's work can neither be regarded as a contribution to the part played by the iron present in chlorophyll, nor as a support to Liebig's theory of the formation of sugar in plants. Since the so-called "isoarabinic acid" bears not the slightest resemblance to arabic acid, it is desirable to rename it. A. R. L.

Derivatives of Sebacic Acid. By R. D. Phookan and F. Krafft (*Ber.*, **25**, 2252—2255).—*Sebacamide*,

$$CONH_2·[CH_2]_8·CONH_2,$$

is obtained when pure pulverised sebacic acid is mixed with phosphoric chloride (2 mol. props.) at the ordinary temperature, and the oily product slowly added to well cooled aqueous ammonia. It is insoluble in water, and only sparingly soluble in alcohol; it crystallises from isobutyl alcohol in minute crystals melting at 208°. On distilling the amide (100 parts) with phosphoric chloride (208 parts), sebaconitrile $C_8H_{16}(CN)_2$, a liquid having a faint fluorescence, a

characteristic penetrating odour, and boiling at 199—200° (15 mm.), is produced. When the nitrile (100 grams) is dissolved in absolute alcohol (2 kilos.), and sodium (350 grams) added, *decamethylenediamine*, $C_8H_{16}(CH_2{\cdot}NH_2)_2$, is formed; the product is acidified with hydrochloric acid, and, after concentrating, the precipitated sodium chloride is removed, the filtrate evaporated to dryness, the residue dissolved in alcohol, and the *hydrochloride* precipitated with ether. The base is obtained by heating the hydrochloride with concentrated alkali; it melts at 61·5°, and boils at 140° (12 mm.). When the hydrochloride is heated at a high temperature, or sublimed under diminished pressure, it decomposes into ammonium chloride and *decamethyleneimine hydrochloride*. The free *base*, $C_{10}H_{20}NH$, of the latter is a liquid of a faint, ammoniacal odour boiling at 104—105° (16·5 mm.); it forms a nitroso-compound which boils at about 160° (15 mm.), and gives Liebermann's reaction. A. R. L.

Ethyl Dioxosuccinate. By R. Anschütz and E. Parlato (*Ber.*, **25**, 1975—1980).—The authors having found, on analysing the so-called ethyl dihydroxytartrate (Abstr., 1891, 725), that it has the formula COOEt·CO·CO·COOEt, propose to name it ethyl dioxosuccinate; it is an orange-yellow liquid of a not unpleasant odour, having a sp. gr. $d\ 20°/4° = 1·1873$, and boiling without decomposition at 115—117° under a pressure of 12 mm., or at 233—234° with slight decomposition at the ordinary pressure, the distillation being usually conducted in a current of hydrogen. A bye-product, boiling at 208—212° (12 mm.), was separated during the rectification. When treated with water (2 mols.), ethyl dioxosuccinate is converted into a colourless liquid, which is perhaps ethyl tetrahydroxysuccinate; after drying over calcium chloride and distilling under a pressure of 12 mm., it gives off water at 70—75°, and is reconverted into ethyl oxosuccinate. A compound, $C_{18}H_{16}N_4O_3$, melting at 154°, and identical with that described by Wislicenus and Scheidt (this vol., p. 458), is obtained when ethyl dioxosuccinate is heated on the water-bath with phenylhydrazine and water. It is also produced when the dihydrazone (m. p. 120°; *loc. cit.*) is boiled with glacial acetic acid.

A. R. L.

Action of Ethyl Salts of Unsaturated Acids on Ethyl Sodiocyanacetate. By P. T. Muller (*Compt. rend.*, **114**, 1204—1207).—When ethyl fumarate and ethyl sodiocyanacetate, in molecular proportion, are heated in presence of excess of alcohol, *ethyl sodiocyanotricarballylate*, COOEt·CH(CHNa·COOEt)·CH(CN)·COOEt, is obtained as a colourless oil which boils at 180—190° under a pressure of 15—20 mm.

When this is treated with dilute sulphuric acid, it yields a liquid, *ethyl cyanotricarballylate*, COOEt·CH(CH_2·COOEt)·CH(CN)·COOEt, which, when boiled for several hours with hydrochloric acid, is decomposed, yielding carbonic anhydride, tricarballylic acid, alcohol, and ammonium chloride. It is the α-derivative, and is isomeric with the β-derivative obtained by Haller and Barthe by the action of ethyl monochloracetate on ethyl cyanosuccinate.

Citraconic acid under similar conditions yields *ethyl methyl-α-cyanotricarballylate*, $COOEt{\cdot}CMe(CH_2{\cdot}COOEt){\cdot}CH(CN){\cdot}COOEt$, which boils at about 190° under a pressure of 15 mm. When saponified with hydrochloric acid, it yields β-methyltricarballylic acid. Like its homologue, β-methyl-α-cyanotricarballylic acid is soluble in alkalis.

C. H. B.

Naphthenes and their Derivatives in the General System of Organic Compounds. By V. Markovnikoff (*J. pr. Chem.* [2], **45**, 561—580).—The first part of a review of our knowledge of the naphthene and naphthylene hydrocarbons. Inasmuch as they differ in many respects both from the aliphatic and aromatic hydrocarbons, the author regards them and their derivatives as constituting a third general class of organic compounds (compare Abstr., 1884, 1276; 1887, 922).

A. G. B.

Tribromonitrobenzene. By C. L. Jackson and W. B. Bentley (*Amer. Chem. J.*, **14**, 363—366).—Tribromonitrobenzene (5 grams) was dissolved in benzene, mixed with an alcoholic solution of sodium ethoxide (1 gram of sodium), heated on the water-bath for some time, and then left at a temperature a little above the ordinary for several hours; the liquid was filtered, water and dilute sulphuric acid were added, and the benzene separated; the aqueous portion was then washed with ether, and the residue from the evaporation of this was mixed with that from the benzene, and crystallised from alcohol. Analysis proved this substance to be *dibromonitrophenetoïl*, $NO_2{\cdot}C_6H_2Br_2{\cdot}OEt$; it crystallises in bundles of white prisms, turns brown in air, and melts at 91°; it is very slightly soluble in water, light petroleum, cold glacial acetic acid, and cold alcohol, and freely soluble in benzene, chloroform, acetone, carbon bisulphide, ether, hot alcohol, and hot glacial acetic acid; it distils with steam. The reaction between tribromonitrobenzene and sodium methoxide appears to yield dibromonitranisoïl.

Tribromonitrobenzene is more stable than tribromodinitrobenzene and tribromotrinitrobenzene, the former of which reacts with sodium ethoxide in the cold to produce bromodinitroresorcinol ethyl ether, whilst with the latter a more deep-seated reaction occurs. Aniline, which readily forms anilido-derivatives with the dinitro- and trinitro-derivatives, is without action on tribromonitrobenzene.

A. G. B.

Synthesis of Dihydroparaxylene. By A. v. Baeyer (*Ber.*, **25**, 2122—2123; compare this vol., pp. 833 and 1074).—When ethyl sodiosuccinosuccinate is treated with methyl iodide, an oil, insoluble in dilute alkalis, and boiling at about 192° (14 mm.), is obtained; the distillate solidifies, forming crystals which melt at 72·5° and have the composition of an *ethyl dimethylsuccinosuccinate*. Inasmuch, however, as this compound gives a phenylhydrazone (m. p. 207°), it may be regarded as ethyl dimethyldiketohexamethylenedicarboxylate,

$$COOEt{\cdot}CMe<\begin{matrix}CH_2{\cdot}CO\\CO{\cdot}CH_2\end{matrix}>CMe{\cdot}COOEt.$$

The compound, when treated with dilute sulphuric acid, behaves in a manner analogous to ethyl succinosuccinate, already described (*loc. cit.*, p. 833), a *dimethyldiketohexamethylene* melting at 93° being formed; this, on reduction, yields a *dihydroxy-compound* (*dimethylquinitol*) in the form of a syrup. The *dibromide*,

$$CHMe<\begin{matrix}CH_2\cdot CHBr\\CHBr\cdot CH_2\end{matrix}>CHMe,$$

obtained from the latter, if heated with quinoline, gives a *dihydroxylene* which is in all probability represented by the formula $CMe<\begin{matrix}CH\cdot CH_2\\CH_2\cdot CH\end{matrix}>CMe$. This boils at about 133—134° under a pressure of 720 mm., has the odour of oil of turpentine, changes the colour of permanganate to brown, gives a crystalline bromo-additive product when treated with bromine water, and decolorises a solution of bromine in chloroform, with evolution of hydrogen bromide. It solidifies in crystals after a while, and gives a yellowish-red colour with alcoholic sulphuric acid; a crystalline nitrosite could not be obtained. It is not possible to decide from these properties whether the dihydroxylene is identical with one of the known terpenes, but, since it behaves as a terpene, the synthesis of the members of the limonene series is to be regarded as a solved problem. The preparation of terpenes derived from cymene can be accomplished by introducing methyl and isopropyl groups into ethyl succinosuccinate.

The author is now studying the action of ethylene bromide and methylene iodide on ethyl sodiosuccinosuccinate. Cantharene is probably a derivative of orthoxylene. A. R. L.

Mechanism of the Formation of Tricyanides from Nitriles and Acid Chlorides in the presence of Aluminium Chloride. By P. Eitner and F. Krafft (*Ber.*, **25**, 2263—2269).—When a mixture of benzoic chloride and aluminium chloride (1 part of each) and benzonitrile (2 parts) is heated for eight hours and then triturated with chloroform, lustrous, prismatic crystals of the *compound* $COPh\cdot N{:}CPh\cdot N{:}CPhCl,AlCl_3$ rise to the surface of the liquid. The compound is very hygroscopic, and dissolves in alcohol with the formation of imidodibenzamide (m. p. 104°) and ethyl benzoate; when, however, the solution is treated with ammonia, a small quantity of kyaphenine (triphenyl tricyanide) is obtained. The latter fact led to the discovery of the following method of preparing kyaphenine:—

Benzonitrile (15 parts), benzoic chloride (8 parts), and well-dried, pulverised ammonium chloride (9 parts) are mixed, and coarsely pulverised aluminium chloride (8·5 parts) added to the mixture at 0° with agitation; after 1—2 hours, the aluminium chloride dissolves, the liquid is heated in an oil-bath for 24 hours at a temperature gradually increasing from 90° to 140°, and finally maintained at 140—150° for a time; hydrogen chloride is evolved, and the product, which solidifies on cooling, is poured into ice-cold water, collected, washed successively with hydrochloric acid, water, and ether, and

subsequently with sodium hydroxide, water, and cold alcohol, when kyaphenine, to the extent of 60 per cent. of the theoretical amount, remains.

In the formation of tricyanides from nitriles, acid chlorides, and aluminium chloride in the absence of ammonium chloride, the nitrile probably undergoes conversion into the amide or ammonium salt by means of the water present in the crude reagents, and this view finds support in the fact that when pure materials are employed, very little tricyanide is produced, whereas a large yield is obtained when a small quantity of water vapour is passed into the mixture.

In the preparation of methyl diphenyl tricyanide (Abstr., 1890, 1252), a yellow, crystalline bye-product is obtained, which yields the tricyanide, and not, as in the above-mentioned case, a dicyanide, on treatment with water. This compound appears not to be an intermediate one in the reaction, and it is formed when aluminium chloride (1 part) is dissolved in acetic chloride (15 parts) at 0° and methyl diphenyl tricyanide added.

The question of the formation of methyl diphenyl tricyanide is still an open one. The authors do not regard the explanation offered by Pinner (this vol., p. 1110) as impossible, but they point out that the benzoylbenzamidine obtained by the latter cannot be an intermediate product of the synthesis, but must result from the decomposition of an intermediate product. A. R. L.

Monosodium Catechol. By de Forcrand (*Compt. rend.*, **114**, 1195—1197).—Sodium (1 equivalent) is dissolved in a cold alcoholic solution of catechol (1 equivalent) in an atmosphere of hydrogen. When solution is complete, the alcohol is dissolved off, and the residue is heated at 120—125° in an atmosphere of hydrogen until quite dry. The monosodium catechol thus obtained is white and crystalline, but rapidly becomes grey when exposed to air, and by prolonged exposure to air or oxygen becomes black.

Heat of dissolution at 15—20° = +1·29; heat of dissolution of catechol −3·46 Cal.

$C_6H_6O_2 + \frac{1}{2}Na_2O$	develops	+ 5·96 Cal.
$C_6H_6O_2$ sol. + Na sol. = H gas + $C_6H_5NaO_2$ sol.	,,	+44·29 ,,
$C_6H_6O_2$ sol. + NaOH sol. = H_2O sol. + $C_6H_5NaO_2$ sol.	,,	+12·42 ,,

These numbers are higher than the corresponding values for phenol, and it would seem that in the case of the polyhydric phenols there is an exaggeration of the apparent value of the first phenolic function, similar to that already observed in the case of the polyhydric alcohols. Moreover the difference between the value of the first function in the case of methyl alcohol and glycol (5·81 Cal.) is practically the same as the corresponding difference between phenol and catechol (5·19 Cal.). C. H. B.

Sodium Resorcinol and Sodium Quinol. By de Forcrand (*Compt. rend.*, **114**, 1370—1373).—The method employed for the

preparation of the sodium compounds of resorcinol and quinol was similar to that adopted in the case of the corresponding compound of catechol (preceding abstract). They are more soluble in alcohol than the catechol compound, and are more rapidly affected by exposure to air. They also retain alcohol more tenaciously, and the resorcinol compound is very hygroscopic.

Heats of dissolution of the two phenols at 20°, resorcinol −3·79 Cal., quinol −4·42 Cal.; heats of dissolution of the sodium compounds, resorcinol +8·82 Cal., quinol +7·01 Cal.; heats of neutralisation by sodium hydroxide in dilute solution, resorcinol +8·23 Cal., quinol +7·50 Cal. It follows that—

$C_6H_6O_2$ sol. + Na sol. = H gas + $C_6H_5NaO_2$ sol.	develops	resorcinol	+38·70 Cal.
		quinol	+39·15 „
$C_6H_6O_2$ sol. + NaOH sol. = H_2O sol. + $C_6H_5NaO_2$ sol. .	„	resorcinol	+ 6·83 „
		quinol	+ 7·28 „

These numbers are practically identical for the two isomerides, and agree with the corresponding numbers for phenol. Combining these results with those obtained in the case of catechol (*loc. cit.*), it is evident that when the two hydroxyl groups are in the meta- or para-positions, the first phenolic function has practically the same value as in ordinary phenol, but when the hydroxyl groups are in the ortho-position there is an apparent exaggeration of the thermal value of the first phenolic function analogous to that observed in the case of glycol.

It is noteworthy that catechol gives the highest number for the heat of neutralisation in the solid state, but the lowest number when the compounds are in dilute solution. This difference may be due to the greater energy with which the sodium salts of resorcinol and quinol combine with the water. C. H. B.

Bimetallic Derivatives of Dihydric Phenols. By DE FORCRAND (*Compt. rend.*, **114**, 1434—1437).—The bimetallic derivatives were prepared in the same way as the mono-derivatives, using, of course, two equivalents of sodium (preceding abstracts).

Disodium catechol is colourless in hydrogen, but when exposed to air becomes first grey, then black, and deliquesces. The resorcinol compound becomes brown, and deliquesces very rapidly in moist air. The quinol compound is slightly coloured, even in hydrogen, and when exposed to air becomes dark blue, and finally black. Heat of dissolution at 20°, catechol compound +12·09 Cal., resorcinol compound +20·51 Cal., quinol compound +20·70 Cal.

		Catechol.	Resorcinol.	Quinol.
NaOH diss. + $C_6H_5NaO_2$ diss.	develops	+ 1·48	+ 7·10	+ 6·18 Cal.
Na_2 sol. + $C_6H_6O_2$ sol..	„	+78·05	+77·19	+74·72 „
Na sol. + $C_6H_5NaO_2$ sol.	„	+33·76	+38·49	+35·57 „

In the case of catechol the total value is 78·05 Cal., and the mean value +39·025 Cal., which is identical with the value for ordinary phenol. The relation between phenol and catechol is, therefore, the

same as between methyl alcohol and glycol. There is an exaggeration of the apparent thermal value of the first phenolic function, and a corresponding reduction of the value of the second function, due to intramolecular combination between the free second function and that in which the substitution of the metal has already taken place. In the case of catechol this combination develops +5·26 Cal., and in the case of glycol +5·67 Cal. when liquid, and 4·34 Cal. when solid.

The thermal values of the two functions of resorcinol are practically identical, but each value, as well as the mean +38·6, is distinctly lower than +39, and the difference is greater than the error of experiment. It follows that the separation of the two C·OH groups by a CH group not only reduces the energy of intramolecular combination, but also reduces the mean energy of the phenolic function.

Quinol behaves partly like catechol and partly like resorcinol. The difference between the apparent values of the two functions +39·15 Cal., +35·57 Cal., indicates intramolecular combination, resulting in a development of +1·79. The mean value of the phenolic function +37·36 Cal. is even lower than in the case of resorcinol.

The value of the phenolic function is only constant when the two OH groups are contiguous, and it diminishes as the separation of the OH groups by hydrocarbon groups becomes greater and greater.

Colson has shown that the heats of neutralisation of the three phthalic acids are as follows: ortho- +53·99 × 2, meta- +52·23 × 2, para- +51·68 × 2; and Massol has shown that similar and greater differences are observed in the case of bibasic organic acids derived from paraffin. C. H. B.

Action of Chlorine on Phenols. By T. Zincke (*Ber.*, **25**, 2219—2236).—A continuation of the study of the products obtained from the so-called heptachlororesorcinol (Abstr., 1891, 691).

The acid $C_6H_2Cl_8O_2$ (*loc. cit.*) is conveniently prepared by adding a dilute solution of bleaching powder to one of the heptachlororesorcinol in a little glacial acetic acid, and subsequently dilute hydrochloric acid, when it separates. The following experiment shows that it is trichloracetopentachlorobutyric acid. When the acid is dissolved in an excess of cold, aqueous soda, and the solution, after a time, acidified with hydrochloric acid, chloroform separates, and *pentachloroglutaric acid*, $CHCl(CCl_2{\cdot}COOH)_2$, is obtained on extracting the aqueous portion with ether. The latter crystallises in small, white needles, containing 1 mol. H_2O, is readily soluble in water, alcohol, and ether, but only sparingly so in light petroleum; when dried at 100°, it melts at 165°. The *methyl salt* melts at 61—62°. The acid $C_6H_2Cl_7BrO_3$, when treated in an analogous manner, yields dichlorobromomethane and pentachloroglutaric acid.

When tetrachlorodiketopentamethylene (*loc. cit.*) is treated in a fused condition with dry chlorine at 200° for 2—3 hours, and the product distilled, *perchloro-β-acetoacrylic chloride*,

$$CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COCl,$$

passes over at 149—150° under a pressure of 17—20 mm. The corresponding acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COOH$, is obtained when the chloride

is heated with dilute hydrochloric acid at 130—140°; it is also formed when the tetrachlorodiketopentamethylene is heated in a sealed tube at 150—160° for some hours with finely-powdered manganese peroxide (1 mol. prop.) and the calculated quantity of hydrochloric acid. It crystallises from light petroleum in small, white needles or leaflets, melts at 83—84°, and is readily soluble in alcohol, ether, and benzene; it also crystallises from hot water with $1\frac{1}{2}$ mols. H_2O. Both the acid and the chloride dissolve in sodium hydroxide solution, with the formation of chloroform and dichloromaleïc acid (m. p. 118—119°). The *amide*, $C_5Cl_5O_2{\cdot}NH_2$, formed when the chloride is carefully treated in the cold with concentrated aqueous ammonia, avoiding excess, crystallises from hot water in colourless, translucent tablets melting at 85—86°, or from benzene in prisms which effloresce on exposure, and then melt at 143°. The *anilide*, $C_5Cl_5O_2{\cdot}NHPh$, obtained when aniline (2 mols.) is added to a solution of the chloride in glacial acetic acid, crystallises from dilute alcohol in white, silky needles, melts at 182—183°, and dissolves in sodium hydroxide solution with decomposition. The corresponding *paratoluidide* melts at 192—193°. When the above-described acid chloride is dissolved in glacial acetic acid, and the solution heated on the water-bath with an excess of aniline, a *compound* separates, which crystallises from benzene in red needles, and melts at 229°; whilst on adding water to the filtrate a *compound* is obtained crystallising from alcohol in the form of yellow nodules melting at 146—147°. These substances are, perhaps, represented by the formulæ

$$\begin{array}{l} NHPh{\cdot}C{\cdot}CO{\cdot}NPh \\ NHPh{\cdot}C{\cdot}CO{\cdot}CO \end{array} \quad \text{and} \quad \begin{array}{l} NHPh{\cdot}C{\cdot}CO{\cdot}NPh \\ NHPh{\cdot}C{\cdot}CO{\cdot}C{:}NPh \end{array}$$

respectively. Two similar compounds, melting at 196° and 152°, are obtained from the chloride and paratoluidine.

On dissolving the amide, $C_5Cl_5O_2{\cdot}NH_2$ (see above), in alcohol, and boiling the solution with aniline, the chief product is a compound which crystallises from alcohol in orange, rhombic leaflets, and melts at 221°; its constitution is possibly $\begin{array}{l} NHPh{\cdot}C{\cdot}CO{\cdot}NH \\ NHPh{\cdot}C{\cdot}CO{\cdot}C{\cdot}NPh \end{array}$.

The compound $C_5Cl_8O_2$, previously described (*loc. cit.*), is obtained when the acid chloride $C_5Cl_6O_2$ (see above) is heated for 8—10 hours in a sealed tube at 200° with phosphorus pentachloride. It is a colourless, highly-refracting oil, boils at 153—154° (12—15 mm.), and is extremely stable, being only attacked by alcoholic potash on boiling with it for a day, when it yields dichloromaleïc acid. As already stated (*loc. cit.*), the compound is decomposed by the continued action of phosphorus pentachloride into hexachlorethane and an oil, C_3Cl_4O; the latter appears, however, to be a solution of hexachlorethane in the unattacked substance. The above facts harmonise best with the constitution $CCl_3{<}\begin{array}{l} CCl{-}{-}CCl \\ O{\cdot}CCl_2{\cdot}CCl \end{array}$ for the compound. A. R. L.

Phenylene Oxide. By W. Vaubel (*J. pr. Chem.* [2], **46**, 51—53). —Märker (*Annalen*, **124**, 249) stated that he had obtained phenylene

oxide, C_6H_4O, by the destructive distillation of salicylosalicylic acid. Goldschmidt (*Jahresberichte*, 1883, 1137), however, failed to recognise it among the products, and the author has also failed to prepare it, not only by the method indicated, but also by heating the dibromobenzenes with zinc oxide, resorcinol with phosphoric anhydride, and hydroquinone with the same dehydrating agent.

Kekulé's formula for benzene will only admit of the existence of one phenylene oxide, for it can only be conceived of as being the anhydride of orthodihydroxybenzene, in which the hydroxyls are adjacent. According to the author's formula for benzene (Abstr., 1891, 1343) it is quite possible for a para- or meta-dihydroxybenzene to yield phenylene oxide. Nor would such a reaction be particularly out of the common, for it is known that pariodophenol yields resorcinol when melted with an alkali (Abstr., 1888, 262), and the same seems to be true of orthiodophenol above 200° (Schall, *Ber.*, **16**, 1897; Abstr., 1883, 1109). If mutual attraction and ability to shift their positions be allowed to the substituting groups in a benzene derivative, the formation of phenylene oxide as an intermediate product in these reactions is to be expected. A. G. B.

Oxidation of Bisecondary Pentethylphloroglucinol by means of Uncombined Oxygen. By B. C. Ulrich (*Monatsh.*, **13**, 245—251).—When pentethylphloroglucinol was allowed to remain for from four to six weeks in a flask containing uncombined oxygen and exposed to light, decomposition occurred (compare Herzig and Zeisel, Abstr., 1888, 247 and 966, and Spitzer, Abstr., 1890, 1110), with the formation of carbonic anhydride, propionic acid, tetrethylacetone, and a small quantity of diethylmalonic acid. When the oxidation was induced by alkaline permanganate, a volatile acid (in all probability propionic acid), was the chief product, but a small quantity of a heavy neutral oil of the formula $C_{15}H_{26}O_2$, boiling at 275—285°, was also formed. This oil must be regarded as the triketone

$$CHEt_2\cdot CO\cdot CEt_2\cdot CO\cdot COEt,$$

since, on further oxidation, it gave, as was expected, a mixture of tetrethylacetone and propionic acid. *Tetrethylacetone*, $C_{11}H_{22}O$, thus obtained, was volatile in a current of steam, boiled at 200—205° (uncorr.), had a characteristic but not unpleasant odour, and did not form a compound with hydrogen sodium sulphite. G. T. M.

Formation of Diphenylamine from Orthobromobenzoic Acid. By A. Heidenreich and V. Meyer (*Ber.*, **25**, 2188—2189).—It has been shown that the bromine is eliminated from orthobromobenzophenone by an alkaline solution of hydroxylamine, and that the oxime of this ketone gives up its bromine when treated with soda. The authors have found that the bromine of orthobromobenzoic acid can also be eliminated by alkalis.

When the bromobenzoic acid is heated with aqueous ammonia in a sealed tube, action takes place at 180°, and is easily completed at 200°. With alcoholic ammonia, the action takes place at 130°. The

product contains only a very small quantity of anthranilic acid, but somewhat notable quantities of salicylic acid and diphenylamine; the latter floats on the aqueous solution as an oil, and is easily separated by steam distillation. The authors believe that the diphenylamine is produced through a diphenylaminecarboxylic acid as represented by the equation $NH_3 + 2C_6H_4Br\cdot COOH = 2HBr + NH(C_6H_4\cdot COOH)_2 = 2CO_2 + NHPh_2$, and on examining the aqueous solution they obtained evidence of the presence of a diphenylaminecarboxylic acid.

Orthobromobenzoic acid is not so easily attacked by other bases as by ammonia, and when boiled for one hour with aniline, the bromine was not eliminated. E. C. R.

Schiff's Bases. By W. v. Miller, J. Plöchl, and others (*Ber.*, **25**, 2020—2071).—Schiff's bases, derived from aromatic aldehydes, have a similar constitution to benzylidenaniline, PhN:CHPh, which serves as the type of these compounds. Most of them are well characterised compounds, and very many have been prepared. Of the bases derived from the fatty aldehydes, a smaller number are known, and only a few of these are well characterised compounds. The authors have prepared Schiff's ethylidenaniline (*Annalen*, **210**, 118), the valeraldehydaniline of Lippmann and Strecker (*Ber.*, **12**, 74), and the anhydroformaldehydaniline (m. p. 140°) of Tollens (*Ber.*, **17**, 657) and Pratesi (*Gazzetta*, **14**, 351).

The molecular weight of these compounds is not yet determined with certainty. The authors, employing Raoult's method, obtained results pointing to the treble formula for anhydroformaldehydaniline, and to the double formula for anhydrovaleraldehydaniline and acetaldehydaniline. Whilst, however, anhydroformaldehydaniline and anhydrovaleraldehydaniline behave in their reactions like the simple base, and are easily split into the same, acetaldehydaniline and propylaldehydaniline behave in an entirely different manner; for they yield acetyl, benzoyl, and nitroso-compounds, and therefore contain an imido-group. Also they unite with bromine and are easily converted into quinoline derivatives. The authors assign to acetaldehydaniline the constitution NPh:CH·CH_2·CHMe·NHPh, and to propylaldehydaniline the constitution NPh:CH·CHMe·CHEt·NHPh. When heated with hydrochloric acid, aniline is eliminated, and the former yields quinaldine, the latter α-ethyl-β-methylquinoline.

A similar polymerisation of the simple base into a bimolecular form of a secondary character has only been observed in the case of the anilide of isobutaldehyde, and then only partially. In all other cases the polymerisation takes place without influencing the tertiary character of the bases. These bases are obtained in their unpolymerised form as oils when formed in the cold, but if allowed to remain for some time they polymerise and become solid. The authors were unable to obtain isomeric forms of the condensation product of aldehyde and aniline as described by Schiff (*Annalen*, Suppl., Bd. **3**, 346).

The authors have examined the behaviour of these compounds towards hydrogen sulphide, reducing agents, and hydrocyanic acid. An easy method of obtaining the nitriles is to dissolve the

amine in ether, add hydrocyanic acid, and then gradually add the aldehyde.

Most of Schiff's bases easily combine with hydrocyanic acid, many of them with avidity. The anilide of acetylcarboxylic acid is an exception, and the reaction takes place with difficulty in the case of the anilide of benzoïn. The authors have also examined the behaviour of hydrazones and oximes towards hydrocyanic acid, and find that the hydrazones and oximes of aldehydes and ketones of the fatty series react with hydrocyanic acid; those of the aromatic series do not.

Thus, as regards the capability of reacting with hydrocyanic acid, Schiff's bases correspond with oximes and hydrazones which contain aliphatic radicles, and the compounds of aniline, phenylhydrazine, and hydroxylamine with acetylcarboxylic acid correspond with hydrazones and oximes which contain aromatic radicles. The authors propose to explain the different behaviour of these similarly constituted compounds by means of space formulæ. The oximes and hydrazones of the fatty series which have exclusively alkyl or hydrogen combined to the carbon atom of the grouping =C=N- are not known to occur in stereomeric forms, nor are Schiff's bases as far as the authors' observations go. The hydrazones and oximes of the aromatic series, however, occur in stereomeric forms. The authors assume that those compounds capable of combining with hydrocyanic acid have a symmetrical configuration, so that the three bonds of the nitrogen atom lie in a plane, and that in those compounds which do not combine with hydrocyanic acid the third bond of the nitrogen atom is not in the same plane as the other two.

Anhydroformaldehydaniline is prepared by mixing aniline with the equivalent quantity of formaldehyde, taking care to keep the mixture cool, and, after some hours, washing the product with water. A mixture is obtained consisting of anhydroformaldehydaniline, which is extracted with benzene, and melts at 140°, and of a crystalline compound quite insoluble in benzene. A determination of the molecular weight of the compound melting at 140° gave numbers pointing to a polymerisation of three molecules of the simple formula PhN:CH_2. The second insoluble compound the authors regard as a higher polymeride, and it gives all the reactions of the less complex compound. When anhydroformaldehydaniline (50 grams) is added with cooling to dry hydrogen cyanide (50 grams), combination takes place slowly, and on remaining over night a crystalline *nitrile* is obtained. This crystallises from a mixture of petroleum and ether in large, white plates, melts at 43°, and is easily soluble in alcohol, ether, and benzene, very sparingly so in petroleum and water. When boiled with concentrated hydrochloric acid for a few minutes, it is converted into phenylglycocoll, $\text{NHPh·CH}_2\text{·COOH}$, which crystallises from water in small, white crystals, and melts at 126°.

Anhydroformaldehydaniline, when suspended in benzene and treated with hydrogen sulphide, yields a compound of the formula $\text{S(CH}_2\text{·NHPh)}_2$, melting at 93°, and also a well crystallised compound which contains sulphur, and melts at 112—117°.

When it is reduced with zinc-dust and concentrated hydrochloric acid, it yields methylaniline.

Condensation of Aniline with Acetaldehyde.—When the equivalent quantity of acetaldehyde is gradually added to aniline dissolved in an equal quantity of 90 per cent. alcohol, and the mixture cooled with ice, a dark yellow oil is precipitated, which soon solidifies. The compound is purified by precipitation with petroleum from its solution in ether. The authors put forward the following formulæ for this compound: $NPh{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}NHPh$ or $NHPh{\cdot}CHMe{\cdot}C_6H_4{\cdot}N{:}CHMe$. It crystallises from ether in large, hexagonal crystals, melts at 126°, boils at 300° without decomposition, and is sparingly soluble in alcohol and benzene, more so in ether. When heated with hydrochloric and acetic acids, it yields quinaldine; it does not combine with hydrocyanic acid or hydrogen sulphide, but yields an acetyl, benzoyl, and nitroso-compound. A determination of the molecular weight by Raoult's method gave numbers agreeing with the above formulæ. The *acetyl compound*, $C_{18}H_{20}N_2O$, crystallises from alcohol, melts at 188°, is soluble in hot alcohol and benzene, sparingly so in ether, and combines with bromine to yield a compound melting at 150—153°. The *benzoyl compound* crystallises in silky leaflets, melts at 218°, and is insoluble in boiling alcohol, ether, and benzene.

The base may also be prepared by adding acetaldehyde to a solution of aniline (21 grams) in water (1000 grams). On allowing the milky liquid to stand for a few days, it deposits a white powder which consists of the above base mixed with the simple base $NPh{:}CHMe$, which is an oil, and reacts with hydrogen cyanide. The nitrile of the oily base is best prepared by adding acetaldehyde to a solution of aniline and hydrocyanic acid in ether. It crystallises from ether or benzene in monoclinic leaflets, melts at 92°, and, when hydrolysed with concentrated sulphuric acid, yields an amide melting at 140°, and then an acid melting at 163°.

Condensation of Propaldehyde with Aniline.—Propaldehyde and aniline, when cautiously mixed, taking care to cool well, yield an oil which solidifies after a time. The solid compound, to which the authors assign the formula $NPh{:}CH{\cdot}CHMe{\cdot}CH(NHPh){\cdot}CH_2Me$ or $NHPh{\cdot}CHEt{\cdot}C_6H_4N{:}CHEt$, melts at 103—104°, is insoluble in water, sparingly soluble in cold alcohol, easily so in ether, benzene, and hot alcohol, and crystallises in white needles. With hydrochloric acid, it yields a sparingly soluble salt. When heated with hydrochloric acid, it is converted into α-ethyl-β-methylquinoline. It does not combine with hydrocyanic acid. The *benzoyl compound* melts at 144—145°, is insoluble in water, and sparingly soluble in petroleum and cold alcohol, easily so in benzene, ether, and hot alcohol.

The simple Schiff's base, propylidenaniline, is obtained by adding the aldehyde to aniline dissolved in ether with cooling. When hydrocyanic acid is added to the ethereal solution thus obtained, the *nitrile* is formed; it is, however, more conveniently obtained by adding the aldehyde to an ethereal solution of aniline and hydrogen cyanide. It crystallises in needles, melts at 39°, is easily soluble in alcohol, ether, and benzene, sparingly in petroleum, and insoluble

in water. When the nitrile is cautiously hydrolysed with sulphuric acid, and the solution diluted with water and saturated with ammonia, α-anilidobutyramide is obtained; this crystallises from alcohol in iridescent scales, melts at 122—123°, is soluble in benzene and ether, somewhat so in hot water, and when treated with hydrochloric acid on the water-bath is converted into α-anilidobutyric acid (m. p. 140—141°).

The *hydrazone*, NHPh·N:CHEt, is prepared by adding propaldehyde to an ethereal solution of phenylhydrazine. When hydrocyanic acid is added to the mixture, the *nitrile* is formed, and on evaporation of the ether and hydrocyanic acid is obtained crystalline. The nitrile is also obtained by adding the aldehyde to an ethereal solution of phenylhydrazine and hydrocyanic acid. It separates in large crystals from a mixture of ether and petroleum, melts at 37°, is insoluble in water, and easily soluble in ether, alcohol, benzene, and chloroform. When hydrolysed with fuming hydrochloric acid, it is converted into *α-phenylhydrazidobutyramide*. The latter crystallises from a mixture of ether and petroleum in slender needles, melts at 79°, is soluble in alcohol, ether, and benzene, reduces ammoniacal silver solution in the cold, and, when hydrolysed by boiling with 5 per cent. sodium hydroxide, is converted into the corresponding acid.

Butylidenaniline is obtained by mixing equivalent quantities of aniline and normal butaldehyde, and cooling the mixture with ice. It is a viscid oil which was not obtained crystalline, and readily reacts with hydrocyanic acid to yield an oily nitrile. The nitrile is, however, more easily obtained by adding butaldehyde to an ethereal solution of aniline and hydrogen cyanide. It solidifies after some time, crystallises from light petroleum in nacreous leaflets, and melts at 51°. Both the crystalline and oily nitrile, when hydrolysed with concentrated sulphuric acid, yield α-anilido-*n*-valeramide (m. p. 99°), and then α-anilido-*n*-valeric acid (m. p. 147—148°).

Isobutaldehyde and aniline yield an oily condensation product which crystallises after a time. The freshly prepared oil combines with hydrogen cyanide to yield a nitrile. The solid base crystallises from petroleum and benzene in white needles, melts at 140°, is easily soluble in ether, alcohol, and benzene, sparingly so in petroleum, insoluble in water, and yields a sparingly soluble salt with hydrochloric acid, and an *acetyl compound* when treated with acetic anhydride. The oily base, when reduced in alcoholic solution with sodium, yields aniline and aldehyde; isobutylaniline could not be detected in the reduction product. The *nitrile*, prepared in the same way as the nitriles mentioned above, crystallises in white needles, melts at 54°, is easily soluble in alcohol, ether, benzene, and hot petroleum, and evolves hydrogen cyanide when warmed with water. When hydrolysed with concentrated sulphuric acid, *α-anilidoisovaleramide* is obtained; this crystallises from benzene in white leaflets, melts at 102—103°, is easily soluble in alcohol, benzene, and ether, sparingly so in petroleum and warm water, and, when melted with aqueous sodium hydroxide, is converted into α-anilidoisovaleric acid melting at 135°.

Anhydrovaleraldehydaniline, $(NPh{:}CH{\cdot}CH_2{\cdot}CHMe_2)_2$, is obtained as described by Lippmann and Strecker (*Ber.*, **12**, 72). When purified by washing with absolute alcohol, it forms a white, crystalline powder, melts at 97°, is very easily soluble in ether, benzene, and chloroform, easily so in toluene, acetone, and hot petroleum, sparingly in cold petroleum and hot alcohol, and insoluble in cold absolute alcohol. It boils at 227°, can be distilled without noticeable decomposition, and is volatile with steam. It does not yield either an acetyl or benzoyl derivative when treated with the usual agents, but is decomposed with formation of acetanilide and benzanilide. When treated with concentrated hydrochloric acid or with zinc chloride, it is converted into α-isobutyl-β-isopropylquinoline. When reduced in amyl alcoholic solution with sodium, it yields isoamylaniline. When reduced in ethyl alcoholic solution with sodium, it yields a compound of the formula $C_2H_2(NHPh)_2(CH_2{\cdot}CHMe_2)_2$; this is a viscid oil, distils at 300—315° without decomposition, and yields a crystalline hydrochloride which is very sparingly soluble in water. The *acetyl derivative* crystallises from light petroleum in large, colourless prisms, and melts at 132°. The *benzoyl derivative* crystallises from light petroleum in colourless tablets, melts at 132—134°, and with sodium nitrite yields a nitroso-compound melting at 118°. The *nitroso-compound* crystallises from light petroleum in concentric needles, and melts at 83—84°.

Anhydrovaleraldehydaniline does not yield additive compounds with hydrogen sulphide or carbon bisulphide; the former converts it into thioaldehyde and aniline, the latter into thiocarbanilide. It is energetically attacked by bromine and iodine in chloroform solution, but the products evolve halogen hydride, and are quickly converted into resin. Neither could any definite compound be obtained by the action of ethyl iodide.

When treated with excess of dry hydrogen cyanide, the *nitrile*, $NHPh{\cdot}CH(CN){:}CH_2{\cdot}CHMe_2$, is obtained; this crystallises from benzene in long, thin prisms, melts at 67°, is volatile with steam, and distils at 210—230° without decomposition. When hydrolysed with concentrated sulphuric acid, it is converted into the corresponding *acid amide*, which melts at 106—107°, and, when boiled with concentrated hydrochloric acid, yields the acid

$$NHPh{\cdot}CH(COOH){\cdot}CH_2{\cdot}CHMe_2.$$

This crystallises in quadratic tablets, melts at 168—170°, and is easily soluble in ether, alcohol, chloroform, and hot benzene.

When treated with 40 per cent. aqueous hydrocyanic acid, it is converted into the *nitrile* of the bimolecular compound of the formula $C_{23}H_{31}N_3$, together with a small quantity of the preceding nitrile. This nitrile forms white, strongly refractive crystals, melts at 136°, is not volatile with steam, and, when distilled at 200—230°, is split into the normal nitrile (m. p. 67°) and the simple base, the latter decomposing.

The unpolymerised base, $NPh{:}CH{\cdot}CH_2{\cdot}CHMe_2$, is obtained by adding the aldehyde to a well cooled solution of aniline in two parts of ether. It remains liquid for some days, and, with

aqueous hydrocyanic acid, gives a very good yield of the normal nitrile.

Isovalerylidenetoluidine is obtained by shaking an ethereal solution of paratoluidine with isovaleraldehyde. It separates from hot alcohol in colourless crystals, and melts at 99°. The *nitrile* is obtained from the crystalline base only by employing a large excess of concentrated hydrocyanic acid, but is easily obtained by the indirect method previously described, and melts at 62—63°. The corresponding *acid amide* melts at 131°; the *acid* at 192°.

Condensation of Œnanthaldehyde with Aniline.—The condensation product of œnanthaldehyde and aniline is a yellow oil having a characteristic odour; it soon polymerises, and cannot be obtained in a solid state. When treated with hydrocyanic acid, large quantities of resin are formed, and the nitrile could not be obtained. The *nitrile* is easily obtained by adding œnanthaldehyde to an ethereal solution of aniline and hydrogen cyanide. It crystallises from alcohol, and melts at 39·8°. The *acid amide* obtained from it crystallises from alcohol in minute, white needles, melts at 105·3°, and when boiled with dilute hydrochloric acid is converted into the corresponding *acid*. The latter is a white, crystalline powder, melts at 147·3°, and when damp is easily decomposed.

Œnanthaldehydehydrazone, when dissolved in ether and treated with excess of concentrated hydrocyanic acid and allowed to remain eight days, yields a very small quantity of nitrile. The *nitrile* is, however, easily obtained by adding œnanthaldehyde to an ethereal solution of phenylhydrazine and hydrogen cyanide, allowing the mixture to remain 24 hours in a closed flask, and distilling off the ether and hydrocyanic acid. After four days the nitrile solidifies. It crystallises from a mixture of alcohol and ether in large, colourless leaflets, and melts at 50·8°.

Phenyl-α-anilidocrotonitrile, NHPh·CH:CH·CHPh·CN, is obtained by gradually adding cinnamanilide to well-cooled hydrocyanic acid. It crystallises from alcohol or benzene in colourless needles, melts at 131°, is easily soluble in alcohol, less so in benzene, insoluble in water and light petroleum, and when boiled with concentrated hydrochloric acid, is converted into phenyl-α-anilidocrotonic acid.

Benzylideneparanitraniline is obtained by heating paranitraniline with twice the theoretical quantity of benzaldehyde for 4—5 hours at 120—130°. It crystallises from acetone in yellowish prisms, melts at 117—118°, and is easily soluble in warm alcohol, acetone, and benzene, more sparingly in the cold solvents, somewhat sparingly in ether and light petroleum. When boiled with dilute acids, it is decomposed with formation of benzaldehyde. It remains unaltered when heated at 120—130° for 48 hours. The *nitrile*, easily obtained by treating it with hydrocyanic acid, melts at 129°, and is easily soluble in warm alcohol and benzene, and in acetone and chloroform, less so in ether, and only sparingly in petroleum. By boiling with water it is slowly decomposed, and very quickly by alkalis, but it is not decomposed by dilute acids.

An additive product of paranitraniline and benzaldehyde is obtained if the nitraniline is dissolved in the benzaldehyde, and the filtered

solution allowed to remain, when it crystallises out as a yellow precipitate. When dried on a porous plate, it melts at 85—86°, is decomposed by washing with ether or other solvents, and cannot be recrystallised. The product is not pure, and contains small quantities of benzoic acid and the preceding anhydro-base.

Diphenylmethyleneaniline, obtained from benzophenone chloride and aniline, crystallises from absolute alcohol in yellow plates, and melts at 112—113°. The *nitrile* is easily obtained by allowing the base to remain with excess of dry hydrogen cyanide. It crystallises from alcohol in slender, radiating needles, melts at 146·5°, is easily soluble in ether, acetone, chloroform, and benzene, more sparingly in alcohol and light petroleum, is not appreciably decomposed when boiled for a short time with water or dilute acids, and dissolves in concentrated sulphuric acid with a beautiful carmine coloration, which disappears on the addition of water with separation of white flocks.

Anhydrocinnamaldehydanisidine is obtained by heating paranisidine hydrochloride and cinnamaldehyde with concentrated hydrochloric acid. It crystallises in yellow leaflets, and melts at 122°. The *nitrile* is easily formed, crystallises in small, white leaflets, melts at 126—127°, is easily soluble in acetone and chloroform, less so in alcohol and benzene, and sparingly so in ether and light petroleum. When boiled with water or dilute acids, it yields cinnamaldehyde, and gives a dark-red coloration with concentrated sulphuric acid.

Anhydrometanitrocinnamaldehydanisidine is obtained in a similar way to the preceding compound. It crystallises in yellow plates, and melts at 127°. The *nitrile* crystallises in yellow leaflets, and melts at 106°.

Action of Hydrogen Cyanide on Hydrazones.—Those hydrazones which do not combine with hydrogen cyanide at the ordinary temperature do not combine with it even when heated at 70—80°. The following hydrazones were found not to combine with hydrogen cyanide, benzaldehydephenylhydrazone, acetylbenzaldehydephenylhydrazone, cinnamaldehydephenylhydrazone, dihydrobenzaldehydephenylhydrazone, benzophenonephenylhydrazone, acetophenonephenylhydrazone, the two forms of the phenylhydrazone of orthonitrophenylglyoxylic acid, and the hydrazone of acetylcarboxylic acid. The following hydrazones combine with hydrogen cyanide: ethylidenephenylhydrazone, ethylidenediphenylhydrazone, propylidenephenylhydrazone, and acetonephenylhydrazone.

The *nitrile of phenylhydrazidopropionic acid*, NHPh·NH·CHMe·CN, is obtained by allowing a mixture of ethylidenephenylhydrazone and excess of hydrocyanic acid to remain at the ordinary temperature; or by gradually adding acetaldehyde to a solution of phenylhydrazine in excess of hydrocyanic acid, and allowing the mixture to remain. It is purified by drying on porous plates, crystallises from a mixture of petroleum and ether in aggregates of colourless needles, melts at 58—59°, and is very easily soluble in alcohol, ether, chloroform, and acetone, easily so in benzene, but only sparingly in light petroleum. It is insoluble in cold water, but dissolves in hot water, and is deposited on cooling in oily drops. It dissolves in dilute hydrochloric and

sulphuric acids, and is precipitated unchanged on adding an alkali. When boiled with dilute acids, hydrogen cyanide is evolved. It reduces Fehling's solution slowly in the cold, and very quickly when boiled with it.

The corresponding *acid amide* is easily obtained by treating the nitrile with fuming hydrochloric acid. It separates from hot water in spear-like crystals, melts at 124—125°, is easily soluble in alcohol, acetone, and hot water, moderately so in chloroform, sparingly in benzene and ether, and insoluble in petroleum. When hydrolysed with dilute sodium hydroxide (sp. gr. = 1·26) it yields phenylhydrazidopropionic acid, NHPh·NH·CHMe·COOH; this crystallises from methyl alcohol in nodular aggregates of very small needles, and melts between 169° and 172°: when heated quickly, it melts at 174°. It reduces Fehling's solution in the cold; when oxidised with ammoniacal copper sulphate solution, it is converted into phenylhydrazineacetylcarboxylic acid.

Ethylidenediphenylhydrazone is obtained by adding an excess of acetaldehyde to a solution of diphenylhydrazine in ether, and allowing the mixture to remain. It crystallises from light petroleum in thick, colourless tablets or short prisms, melts at 60—61°, and is easily soluble in the ordinary solvents, with the exception of water. It does not dissolve in dilute hydrochloric or sulphuric acid, but when boiled with somewhat concentrated hydrochloric acid, it dissolves with a yellow coloration; in concentrated sulphuric acid it dissolves with a yellow coloration, which quickly changes to yellowish-green, green, bluish-green, and finally pure blue. When treated with hydrocyanic acid, it yields a *nitrile;* this crystallises in thin, colourless tablets, melts at 65°, and is easily soluble in the ordinary solvents, with the exception of water and light petroleum.

The nitrile of phenylhydrazidopropionic acid agrees in its properties with the compound obtained by Reissert (*Ber.*, **17**, 1453) from ethylidenecyanhydrin and phenylhydrazine, and on comparing these products they were found to be identical.

Ethyl anilacetoacetate, when treated with hydrocyanic acid, yields a thick yellow oil, which on being hydrolysed gave the corresponding acid amide. The latter crystallises from alcohol in white, lustrous leaflets, and melts at 163°.

Anilbenzoïn and hydrocyanic acid yield an oily nitrile, which on hydrolysis gives an acid amide. The latter crystallises from dilute alcohol, and melts at 166°.

Ethylmethylketoxime gives a yellow, oily nitrile, which on hydrolysis yields a crystalline compound melting at 57°.

The oxime of acetaldehyde combines with hydrogen cyanide to yield an oily *nitrile*, which soon solidifies; it crystallises from a mixture of ether and petroleum, melts at 97°, and is easily soluble in alcohol, acetone, and water, more sparingly in ether and benzene, and insoluble in petroleum.

Acetoxime yields a nitrile of the formula $C_4H_8N_2O$, which crystallises from ether in large, monoclinic tablets, and melts at 98·5°.

Ethylphenylhydrazine acetoacetate yields a *nitrile*, which crystallises from benzene in needles, and melts at 110°. E. C. R.

Diacetylorthodiamines. By A. Bistrzycki and F. Ulffers (*Ber.*, **25**, 1991—1995; compare Abstr., 1890, 1115).—*Dinitrodiacetyldiamidotoluene*, $C_6HMe(NO_2)_2(NHAc)_2$, is prepared by treating a mixture of diacetylorthodiamidotoluene [Me : $(NHAc)_2$ = 1 : 3 : 4] (2 grams) and carbamide nitrate (0·4 gram) at 0° with the strongest colourless nitric acid, then heating the mixture at 40° for 25 minutes, and, after cooling, pouring it into water. The precipitated compound is fractionally crystallised from alcohol, the least soluble portion being the dinitro-derivative, which when pure forms white, silky needles, melts at 251—252°, and is more readily soluble in glacial acetic acid than in alcohol, but insoluble in water. It forms metallic derivatives which are orange-red or yellow; these are stable towards water, but are decomposed by acids, even by carbonic acid.

Ethenyldinitrotoluyleneamidine, $C_6HMe(NO_2)_2<^{-N}_{NH}>CMe$, is formed by dissolving the last-described compound in 70 per cent. sulphuric acid at 90°, diluting, and neutralising, when the compound separates; it crystallises from benzene in long, lemon-yellow prisms, melts at 219°, and is insoluble in water; it dissolves, moreover, in both acids and alkalis, in the latter case forming metallic derivatives.

Nitrodiacetylorthodiamidotoluene is obtained when a solution of diacetyldiamidotoluene [Me : $(NHAc)_2$ = 1 : 3 : 4] in glacial acetic acid ($7\frac{1}{2}$ parts) is mixed in the cold with concentrated sulphuric acid (10 parts), and potassium nitrate (0·5 part) is dropped by degrees into the mixture heated to 45°. The compound, precipitated by pouring the solution into water, is crystallised from dilute acetic acid; it forms long, yellowish-white needles, melts at 239°, is insoluble in water, and more readily soluble in alcohol than in glacial acetic acid. Its compounds with metallic bases are of various shades of yellow.

Ethenylnitrotoluyleneamidine, $C_6H_2Me(NO_2)<^{-N}_{NH}>CMe$, is prepared from the last-described compound by the method already given under the corresponding dinitro-derivative; it crystallises from water with 1 mol. H_2O, and has the properties already ascribed to it by Niementowski (Abstr., 1886, 545); it, moreover, forms salts with acids and metallic bases, the latter having a red or yellow colour.

Nitrodibenzoylorthodiamidotoluene, $C_6H_2Me(NO_2)(NHBz)_2$, is obtained by heating the dibenzoyldiamidotoluene [Me : $(NHBz)_2$ = 1 : 3 : 4] with a mixture of glacial acetic acid and nitric acid at 45°; it crystallises from glacial acetic acid in white needles, melts at 246°, is insoluble in water, and only slightly soluble in alcohol.

Benzenylnitrotoluyleneamidine, $C_6H_2Me(NO_2)<^{-N}_{NH}>CPh$, is formed when the compound just described is heated in a sealed tube for six hours with alcoholic potash at 110—130°; it crystallises from dilute alcohol in small, brownish-yellow tufts of needles containing water of crystallisation (about $1\frac{1}{2}$ mols.), melts at 222—223°, and is insoluble in water, sparingly soluble in benzene, but readily in alcohol and glacial acetic acid. It behaves towards acids and alkalis like the ethenyl derivative (see above). A. R. L.

Reduction of Symmetrical Triamidotrinitrobenzene. By A. W. Palmer (*Amer. Chem. J.*, **14**, 377—380).—The reduction of triamidotrinitrobenzene results in the replacement of at least one amido-group or one nitro-group by hydrogen (compare Nietzki, Abstr., 1887, 476, 929). Pentamidobenzene trihydrochloride was the only product which could be identified (Abstr., 1888, 1276; 1890, 247).

A. G. B.

Dinitrosoazobenzene. By F. Kehrmann (*J. pr. Chem.* [2], **46**, 53—56).—Kehrmann defends himself against Willgerodt's animadversions (this vol., p. 1079). A. G. B.

New Synthesis by means of Diazo-compounds. By R. Hirsch (*Ber.*, **25**, 1973—1975; compare Abstr., 1891, 437).—Aniline (50 grams) is dissolved in 30 per cent. hydrochloric acid (150 grams), and diluted to 400 c.c., the ice-cold solution being then diazotised with sodium nitrite (39 grams), dissolved in water (100 c.c.), and subsequently mixed with aniline (950 grams); on rendering the solution alkaline, drying the oil which separates with calcium chloride, and heating it at 150°, nitrogen is evolved, and by carefully raising the temperature to 190°, the greater portion of the aniline distils over; when the boiling point is 200°, the distillation is stopped, and the residue boiled with water (10 parts) and neutralised with hydrochloric acid. Sodium hydroxide is now cautiously added, and the oil which floats on the surface of the liquid, and consists of amidoazobenzene dissolved in diphenylamine, is removed with bibulous paper; on adding sodium sulphate, paramidodiphenyl sulphate is precipitated and can be collected; the filtrate from this is rendered strongly alkaline, and the oil which separates fractionated, the portion passing over at 275° being almost pure orthamidodiphenyl. When the above-given quantities are employed, the yield is about 45 grams of amidodiphenyl, 900 grams of aniline being recovered. Heussler (Abstr., 1891, 555) has likewise observed the formation of amidodiphenyl by the decomposition of diazoamidobenzene. Amidoazobenzene is formed in not inconsiderable quantity when a solution of diazobenzene is heated with quinoline, but the mechanism of the reaction is not clear.

A. R. L.

Parahydroxyalkyl Derivatives of Phenylhydrazine, &c. By J. Altschul (*Ber.*, **25**, 2185).—Groll claims to have described (*Inaug. Diss., Basel*, 1888) sodium paraethoxydiazobenzenesulphonate and paraethoxyphenylhydrazinesulphonate, which have been lately obtained by the author (this vol., p. 1080). Groll's observation (*loc. cit.*) that these salts cannot be obtained in the anhydrous condition is incorrect. A. R. L.

Action of Nitrous Acid on certain Unsaturated Aromatic Compounds. By A. Angeli (*Ber.*, **25**, 1956—1963).—The *compound* (m. p. 124°) obtained from isosafrole (this vol., p. 44) is probably a dioxime peroxide, $\begin{matrix} O{\cdot}N{:}C{\cdot}C_6H_3{:}O_2{:}CH_2 \\ | \\ O{\cdot}N{:}CMe \end{matrix}$; it is insoluble in alkalis, and, when heated at 210° with acetic anhydride, is converted into a colourless modification which melts at the same temperature; as

both substances give the same nitro-derivative, it is difficult to decide whether they are different compounds. The dioxime peroxide, on oxidation with potassium permanganate, gives piperonylic acid and other products; and on reduction with tin and hydrochloric acid, it gives a compound which crystallises from alcohol in white needles and melts at 86°; it probably has the constitution

$$O<\begin{matrix}N:C\cdot C_6H_3:O_2:CH_2\\ |\\ N:C\cdot Me\end{matrix};$$

on reduction with zinc and acetic acid, on the other hand, two compounds are obtained, one, probably $CH_2:O_2:C_6H_3\cdot CH_2\cdot COMe$, crystallises in white needles and melts at 38°, the other, $C_{20}H_{18}N_2O_4$, melts at 180°. The keto-compound (m. p. 38°) forms a phenylhydrazone melting at 97°. When the dioxime peroxide is dissolved in alcohol, and carefully reduced with zinc-dust and dilute acetic acid, the dioxime (?), $CH_2:O_2:C_6H_3\cdot C(NOH)\cdot CMe:NOH$, is produced; it crystallises from benzene in colourless prisms and melts at 159°. It is soluble in alkalis, forms a *diacetyl* derivative melting at 138°, and is reconverted into the peroxide on oxidation with potassium ferricyanide in dilute alkaline solution. On treatment with nitrous acid, isobutenylbenzene yields a *nitrosite*, $C_{10}H_{12}N_2O_3$, melting at 112°. When isosafrole dioxime peroxide (see above) is treated with alcoholic potash, an *isomeride* is obtained melting at 185° with decomposition; it dissolves in alkali hydroxides, but not in carbonates, forms an acetyl derivative melting at 129°, a *benzoyl* derivative melting at 146°, and, on oxidation with potassium permanganate, yields piperonylic acid and its nitrile, together with piperonylcarboxylic acid.

A. R. L.

Orthochlorobenzaldoximes. By R. Behrend and D. Nissen (*Annalen*, **269**, 390—403).—Although anti-benzaldoxime, and all those of its meta- and para-substitution products which have been investigated, are converted into the corresponding syn-oximes by hydrogen chloride, it has not hitherto been found possible to bring about such an intramolecular change in the case of the ortho-substitution products of benzaldoxime; the authors have now succeeded in preparing the two modifications of orthochlorobenzaldoxime by the method previously employed by Behrend and König in the case of paranitrobenzaldoxime (compare Abstr., 1891, 1032).

β-Dichlorobenzylhydroxylamine, $OH\cdot N(CH_2\cdot C_6H_4Cl)_2$, is formed when orthochlorobenzyl chloride (2 mols.) is boiled with an alcoholic solution of hydroxylamine; it separates from alcohol in colourless, granular crystals, and melts at 116—117°. The *hydrochloride* crystallises in needles, melts at 135—155°, and is only very sparingly soluble.

Orthochlorobenzylisoorthochlorobenzaldoxime,

$$C_6H_4Cl\cdot CH_2\cdot N<\overset{O}{\_}>CH\cdot C_6H_4Cl,$$

can be obtained by oxidising the preceding compound with potassium dichromate and acetic acid; it crystallises from a mixture of ether and light petroleum in long needles, melts at 98—99°, and is decom-

posed by hydrochloric acid into chlorobenzaldehyde and β-chlorobenzylhydroxylamine hydrochloride.

β-Chlorobenzylhydroxylamine, $C_6H_4Cl\cdot CH_2\cdot NH\cdot OH$, prepared by decomposing the hydrochloride with sodium carbonate, crystallises from a mixture of ether and light petroleum in lustrous, rectangular plates, melts at 72—74·5°, and reduces Fehling's solution. The *hydrochloride*, C_7H_8ClNO,HCl, separates from alcoholic ether in prismatic crystals, melts at 153—158°, and is very readily soluble in alcohol and water. The *nitroso*-derivative, $C_6H_4Cl\cdot CH_2\cdot N(NO)\cdot OH$, is obtained when β-chlorobenzylhydroxylamine hydrochloride is treated with sodium nitrite in ice-cold solution; it separates from ethereal light petroleum in long prisms, melts at 48—49°, and gives Liebermann's reaction.

Dinitrosylorthochlorobenzyl, $C_{14}H_{12}Cl_2N_2O_2$, is formed, with evolution of nitrogen, when the nitroso-compound just described is dissolved in a mixture of ether and glacial acetic acid, and a trace of fuming nitric acid added to the solution; it crystallises from a mixture of chloroform and ether in needles, melts at 115·5—117°, and is only sparingly soluble in ether and alcohol; it gives Liebermann's reaction.

When dinitrosylorthochlorobenzyl is treated with 10 per cent. soda, and the mixture kept for several days, it is partially converted into approximately equal quantities of syn- and anti-orthochlorobenzaldoxime; on largely diluting the filtered solution and then passing a stream of carbonic anhydride, the more sparingly soluble syn-oxime is deposited, whilst the anti-oxime (m. p. 75—76°) remains in solution.

Synorthochlorobenzaldoxime, C_7H_6ClNO, melts at 98—102°, and in appearance is not to be distinguished from the anti-oxime; both compounds crystallise in small, slender needles, and dissolve freely in the ordinary organic solvents, except light petroleum; they are both decomposed by sulphuric acid into hydroxylamine and chlorobenzaldehyde. The syn-oxime is very readily converted into the anti-modification, not only by hydrogen chloride, but also by dilute acids. When the syn-oxime is dissolved in acetic anhydride, it yields an unstable *acetyl* derivative which, on treatment with sodium carbonate, even in the cold, is quickly converted into chlorobenzonitrile; the acetyl derivative of the anti-oxime melts at 84—88°, and is not acted on by sodium carbonate. F. S. K.

Aromatic Alkyl Ketoximes containing a Halogen Atom in the Ortho-position relatively to the Ketoxime Group. By A. Claus (*J. pr. Chem.* [2], **46**, 20—50; compare this vol., p. 985; Abstr., 1890, 769, 979; 1891, 199, 564, 1222).—*Parabromometatolyl methyl ketone* [Me : COMe : Br = 1 : 3 : 4] is a colourless, mobile, refractive liquid of aromatic odour; it boils at 262° (corr.), is slightly volatile with steam, is still liquid at −20°, and dissolves in the usual organic solvents, but hardly at all in water. The *ketonic acid*, obtained by oxidising it with alkaline potassium permanganate, melts at 54°. The acid obtained by its further oxidation melts at 154—155° (uncorr.), and is undoubtedly bromomethylbenzoic acid

[Me : COOH : Br = 1 : 3 : 4]

(compare Beilstein, 2nd Edition, **2**, 858; the barium salt crystallises with 4 mols. H_2O), for it is converted by still further oxidation into 4-bromisophthalic acid [$(COOH)_2 : Br = 1 : 3 : 4$] (m. p. 287°, uncorr.; Abstr., 1891, 1222).

The conversion of brominated ketones, in which the bromine is in the meta- or para-position relatively to the ketone group, into oximes, takes place in the absence of alkalis, the ketone being merely heated with hydroxylamine hydrochloride in dilute alcohol; it is otherwise when the bromine is in the ortho-position relatively to the ketone group, the presence of alkalis being then necessary, and the product less pure.

Parabromometatolyl methyl ketoxime [Me : CMe : N·OH : Br = 1 : 3 : 4] crystallises in brilliant, large, transparent, rectangular tables when its alcoholic solution is gradually evaporated, and in needles and quadratic prisms when the hot solution is cooled; it melts at 109° (uncorr.). By treatment with sulphuric acid, it is converted into the isomeric *parabromometacetotoluidide* [Me : HN·COMe : Br = 1 : 3 : 4], which melts at 164° (uncorr.), and therefore differs from Neville and Winther's compound (*Ber.*, **13**, 972). By saponification with alkali and distillation with steam, the toluidide yields parabromometatoluidine [Me : NH_2 : Br = 1 : 3 : 4]; this is characterised by its intense odour of naphthalene, and, with this exception, is identical with Neville and Winther's bromotoluidine (*loc. cit.*).

Parachlorometatolyl methyl ketone [Me : COMe : Cl = 1 : 3 : 4] is a colourless, aromatic, refractive oil boiling at 239—240° (uncorr.), and soluble in the usual organic solvents. By oxidation with aqueous potassium permanganate, it yields *parachlorometatoluic acid*

[Me : CO_2H : Cl = 1 : 3 : 4],

which crystallises in colourless needles, sublimes easily, and melts at 167° (uncorr.). By further oxidation this is converted into *parachlorisophthalic acid* [Cl : $(CO_2H)_2$ = 4 : 1 : 3], which crystallises in colourless needles, melts at 286° (uncorr.), and sublimes; it dissolves easily in hot water, and is not volatile with steam. This chlorisophthalic acid is identical with that described by Claus and Neukranz, who, however, asserted that it does not melt below 340°.

Parachlorometatolyl methyl ketoxime [Me : CMe : N·OH : Cl = 1 : 3 : 4] crystallises in brilliant, quadratic tables and prisms, when its alcoholic solution is slowly evaporated, and in colourless needles when the hot solution is cooled; it melts at 94° (uncorr.), and is not attacked by hot alkalis.

Parachlorometacetotoluidide [Me : HNCOMe : Cl = 1 : 3 : 4] is obtained by the action of sulphuric acid on the ketoxime; it forms colourless needles or columns, and melts at 124° (uncorr.); when deacetylised, it is converted into *parachlorometatoluidine* [Me : NH_2 : Cl = 1 : 3 : 4], which is a colourless oil boiling at 230° (uncorr.), and solidifying to a crystalline mass which melts about 32°; it is characterised by its naphthalene-like odour.

Parachlorometa-1 : 2-*xylyl methyl ketone* [Me_2 : COMe : Cl = 1 : 6 : 3 : 4] is easily obtained by acetylising 4-chloro-1 : 2-xylene

(Abstr., 1885, 1053) with a considerable excess of the usual reagents (aluminium chloride, 3 parts; acetic chloride, 2 parts; chloroxylene, 1 part); it is a colourless, aromatic oil, boils at 275—276° (uncorr.), dissolves in the usual solvents, and soon becomes coloured in light and air. The corresponding *ketoxime* [Me_2 : CMe : N·OH : Cl = 1 : 6 : 3 : 4] crystallises in colourless columns and needles; it melts at 134° (uncorr.), and is somewhat soluble in hot water; it is not attacked by hot alkalis. The corresponding *acetoxylide*

[Me_2 : HNCOMe : Cl = 1 : 6 : 3 : 4],

easily obtained by heating the ketoxime with sulphuric acid, crystallises in colourless, slender prisms, melts at 154° (uncorr.), and dissolves sparingly in hot water; on saponification, it yields *chlororthoxylidine* [Me_2 : NH_2 : Cl = 1 : 6 : 3 : 4] which crystallises in white laminæ, melts at 86° (uncorr.), sublimes, and dissolves easily in the usual organic solvents.

The corresponding compounds from 3-chloro-1 : 2-xylene, namely, the *methyl ketone* (m. p. 278—279°, uncorr.), the *ketoxime* (m. p. 126°, uncorr.), the *acetoxylide* (m. p. 186°, uncorr.), and the *chlororthoxylidine* (m. p. 73°, uncorr.), are here briefly mentioned; they will be further discussed.

The fact that the oximes here described do not lose hydrogen halide when heated with alkalis, proves that the halogen atom is directly united to the benzene nucleus, and is not associated in any way with the oxime hydrogen atom. This observation is contrary to that of Cathcart and V. Meyer (this vol., p. 992), who found that the oxime of orthobromobenzophenone is easily decomposed by alkalis, with elimination of hydrogen bromide. On this peg the author hangs a discussion of the structure of oximes, questioning some of Cathcart and Meyer's theories. An appendix contains a reply to a recent article by Hantzsch on these matters (this vol., p. 1083).

A. G. B.

Configuration of γ-Ketoximic Acids. By W. Dollfus (*Ber.*, **25**, 1926—1936).—γ-Ketoximic acids appear to exist in one stable modification only; as an example, levulinic oxime (Abstr., 1884, 1129) may be cited. This oxime is probably represented by the configuration $Me{\cdot}\overset{\overset{N{\cdot}OH}{\|}}{C}{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ (methylsynketoximepropionic acid); when hydrogen chloride is passed into its ethereal solution, it forms a hydrochloride, which decomposes on treatment with soda, yielding the original oxime. The *acetyl* derivative, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}NOAc$, is obtained by adding the calculated quantity of acetic anhydride to the oxime; it melts at 74—75°, and also yields the original oxime when decomposed with soda. The formation of methylsuccinimide observed by Bredt and Böddinghaus (Abstr., 1889, 1061) is probably preceded by intramolecular change.

Benzoylpropionic acid is prepared according to Burker's directions (*Ann. Chim. Phys.* [5], **26**, 435) by the condensation of benzene with succinic anhydride in the presence of aluminium chloride. The *oxime*,

$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CPh{:}NOH$, is obtained when the acid is dissolved in dilute sodium hydroxide solution, and treated with hydroxylamine hydrochloride ($1\frac{1}{2}$ parts); it crystallises from hot water in long, spear-shaped needles, melts at 129°, and behaves similarly to levulinic oxime. The *acetyl* derivative melts at 99°, and may be crystallised from hot water or dilute alcohol without decomposition; it decomposes into the oxime when boiled with water or soda. When the oxime (m. p. 129°) is allowed to remain in contact with concentrated sulphuric acid for about two days, it slowly dissolves; on now diluting the solution with ice water in such a manner that the temperature does not rise much above 0°, an isomeric *oxime*, melting at 95—96°, is precipitated. It is probably phenylantiketoximepropionic acid,

$$\begin{matrix} Ph{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}COOH, \\ \| \\ HO{\cdot}N \end{matrix}$$

and when exposed to the air it changes into the stable modification (m. p. 129°).

Trichloracetylacrylic acid (Kekulé and Strecker, Abstr., 1884, 1122) is decomposed by alkalis, and cannot, therefore, be converted into its oxime in alkaline solution. If an alcoholic solution of hydroxylamine hydrochloride (12 grams) is converted into the base by means of sodium ethoxide, ether added, trichloracetoacrylic acid (10 grams) dissolved in the filtrate, and the solution then placed in a vacuum, crystals separate which are insoluble in water, alcohol, and ether, and are successively washed with these liquids; they darken at 115° and melt at about 140°, but are found on analysis to be neither the oxime nor its anhydride. The compound is being further investigated. A. R. L.

Amidotolylurethane. By H. Schiff (*Ber.*, **25**, 2210—2212).—The author has already described a method of preparing amidotolylurethane from paranitrotoluidine. He finds that it is more easily prepared from acetyltoluylenediamine, $C_6H_3Me(NH_2){\cdot}NHAc$ [1 : 2 : 4].

The acetyl compound (20—30 grams) is suspended in 8—10 times the quantity of dry ether and 3 c.c. of ethyl chloroformate added to the mixture for every 10 grams of the acetyl compound. In $1\frac{1}{2}$—2 hours a crystalline magma is obtained which contains acetamidotolylurethane and acetyltoluylenediamine hydrochloride. The ether is distilled off and the hydrochloride washed out with very dilute hydrochloric acid. *Acetamidotolylurethane* crystallises in long, colourless, lustrous needles, melts at 181°, and is easily soluble in alcohol, sparingly so in hot water. Amidotolylurethane is obtained by gradually adding it to boiling hydrochloric acid and precipitating the solution with sodium carbonate. Amidotolylurethane is volatile with steam, and melts at 95°, and not at 91° as previously stated. E. C. R.

Mandelamide. By G. Pulvermacher (*Ber.*, **25**, 2212—2213).—By the action of fuming hydrochloric acid on the nitrile of mandelic acid, the author has obtained the condensation product

$$OH{\cdot}CHPh{\cdot}CO{\cdot}N{:}CHPh,$$

already described by Michael and Jeanprêtre (this vol., p. 1088), which melts at 194°, and has been described as mandelamide by Tiemann and Friedländer (*Ber.*, **14**, 1967). A small quantity of mandelamide is found in the mother liquors of the above compound. Mandelamide melts at 132°. Biedermann has described it as melting at 190°, but on preparing the amide according to Biedermann's directions by the action of alcoholic ammonia on the α-lactone of mandelic acid, the author obtained a product melting at 132°. E. C. R.

Modes of Formation of Substituted Imides. By A. Haller (*Compt. rend.*, **114**, 1326—1329).—When a mixture of phthalic acid (1 mol.) and phenyl isocyanate (2 mols.) is gradually heated, carbonic anhydride is evolved and the mixture melts entirely at about 200°. As soon as the evolution of gas ceases the product is allowed to cool, and is crystallised from alcohol; phenylphthalimide is thus obtained in slender, white, silky needles melting at 209°.

Succinic acid, under similar conditions, yields phenylsuccinimide in small, white needles melting at about 154°.

The formation of substituted phenylimides under these conditions would seem to be due to the formation of an anhydride and symmetrical diphenylurea, which afterwards interact with production of the substituted imide, aniline, and carbonic anhydride.

This view is supported by the fact that phthalic anhydride or succinic anhydride, when heated with symmetrical diphenylurea in molecular proportion, yields phenylphthalimide or phenylsuccinimide, as the case may be. The reaction is quantitative, and only traces of secondary products are formed.

Symmetrical orthoditolylurea reacts in a similar way with phthalic anhydride at 200°, and yields orthotolylphthalimide, which crystallises from alcohol in small, white crystals, melts at 174°, and is only slightly soluble in cold alcohol or cold ether.

Attempts to obtain tetra-substituted imides by an analogous reaction gave negative results. Tetraphenylurea and phthalic anhydride remain unchanged when heated together at 150°, 180°, 200°, and even 350°.

Methyl hydrogen phthalate and methyl hydrogen succinate, when heated with phenyl isocyanate in molecular proportion, yield phenylphthalimide and phenylsuccinimide respectively.

Methyl hydrogen phthalate is easily obtained by dissolving phthalic anhydride in absolute methyl alcohol and distilling off the excess of alcohol. It crystallises in white plates, melts at 85°, and dissolves in most solvents except water. The ease with which the salt can be obtained in a state of purity, and the equally great facility with which the phthalic acid, separated by saponification, can be reconverted into phthalic anhydride, make methyl hydrogen phthalate an excellent compound from which to prepare pure methyl alcohol.

Methyl hydrogen succinate is obtained in a precisely similar manner. It crystallises in transparent, rectangular tables, very soluble in ether or alcohol. C. H. B.

Metallic Compounds of Aromatic Ketones. By E. Louise and Perrier (*Compt. rend.*, **114**, 1377—1379).—Ketones unite with anhydrous metallic chlorides to form coloured, solid compounds, sometimes amorphous, but more frequently crystalline.

A solution of the ketone in carbon bisulphide is heated at about 40° in a vessel furnished with a reflux condenser, and anhydrous ferric or aluminium chloride in molecular proportion is gradually added. On cooling, the solid products separate; they alter rapidly in moist air. As a rule, the compounds form most readily when the ketones are in the nascent state, and are being produced at a low temperature, by the method of Friedel and Crafts, in presence of carbon bisulphide. The compound of benzoylmesitylene and aluminium chloride, for example, is most readily obtained in crystals by the addition of aluminium chloride to a solution of mesitylene and benzoic chloride in carbon bisulphide.

The formation of crystalline compounds with aluminium chloride under these conditions makes it possible to isolate ketones readily, and to separate those that are formed in different stages of the reaction. In this way, new ketones formed by the action of acid chlorides on anthracene, phenanthrene, acenaphthene, fluorene, stilbene, diphenylnaphthalene, mesitylene, &c., have been isolated.

Benzoyl-retene is obtained by prolonged boiling of a carbon bisulphide solution of benzoic chloride and retene in molecular proportion to which aluminium chloride has been added gradually. The metallic compound is decomposed by water, and the benzoyl-retene crystallised from light petroleum; it melts at 114°. C. H. B.

Dibromobenzoic Acids. By A. Claus and A. Weil (*Annalen*, **269**, 216—224).—The authors have prepared and characterised four of the dibromobenzoic acids.

Nitrodibromacetanilide [NHAc : Br_2 : NO_2 = 1 : 3 : 5 : 4] is formed, together with a much larger quantity of the corresponding 1 : 3 : 5 : 2-derivative, when dibromacetanilide (m. p. 215°) is nitrated with ice-cold acid of sp. gr. 1·5; it sublimes in small, lustrous plates, melts at 270—271°, and crystallises from alcohol in hexagonal plates, but is insoluble in water.

Nitrodibromaniline [NH_2 : Br_2 : NO_2 = 1 : 3 : 5 : 4], prepared by heating the acetyl derivative with moderately concentrated sulphuric acid at 120—125°, sublimes in lustrous, yellow needles, and melts at 186°; when treated with sodium nitrite and concentrated sulphuric acid in ice-cold alcoholic solution, and the mixture then heated on the water-bath, it is converted into dibromonitrobenzene (m. p. 84°), from which, by reducing with stannous chloride and hydrochloric acid in alcoholic solution, dibromaniline (m. p. 81°), identical with the compound (m. p. 83—84°) prepared by Heinichen (Abstr., 1890, 165), can be obtained.

Dibromobenzonitrile [Br_2 : CN = 3 : 5 : 4], prepared from dibromaniline (m. p. 81°), crystallises in colourless needles, melts at 151°, and is volatile with steam. The corresponding *acid*, obtained by hydrolysing the nitrile with moderately concentrated sulphuric acid at 170°, crystallises and sublimes in small, lustrous needles, melts at

189°, and is readily soluble in alcohol, ether, chloroform, and hot water, but almost insoluble in cold water. The *barium* salt crystallises in slender needles containing 3 mols. H_2O, and is readily soluble in water.

Dibromobenzonitrile [CN : Br_2 = 1 : 2 : 4], prepared from the corresponding dibromaniline, crystallises from alcohol in long, colourless needles melting at 79—80°; on hydrolysis with sulphuric acid, it yields dibromobenzoic acid (m. p. 166·5°), the *barium* salt of which crystallises in needles containing 3 mols. H_2O, and is very readily soluble in water.

Dibromobenzonitrile [CN : Br_2 = 1 : 2 : 5], prepared from the corresponding dibromaniline, crystallises from alcohol and hot water in long, yellowish needles, and melts at 132°. The corresponding acid crystallises in flat, colourless needles melting at 153°; its barium salt crystallises from 90 per cent. alcohol in small plates containing $1\frac{1}{2}$ mols. H_2O, and from water in needles containing 6 mols. H_2O, or in small plates containing $2\frac{1}{2}$ mols. H_2O.

Dibromobenzonitrile [CN : Br_2 = 1 : 3 : 5] crystallises from alcohol in lustrous, colourless needles, melts at 89°, and is readily volatile with steam. The corresponding *acid* crystallises from boiling water in flat, colourless needles, melts at 209°, and sublimes readily; its *barium* salt is not very readily soluble in water and crystallises in small, colourless needles containing 4 mols. H_2O. F. S. K.

Dichlorobenzoic Acids. By A. Claus and A. Stavenhagen (*Annalen*, **269**, 224—231).—*Dichlorobenzonitrile* [CN : Cl_2 = 1 : 3 : 5] prepared from the corresponding dichloraniline, separates from solvents and sublimes in long colourless needles, melts at 65°, and is very readily soluble in alcohol, ether, and chloroform, but insoluble in cold water; it is moderately easily volatile with steam. When hydrolysed with moderately concentrated sulphuric acid, it is converted into dichlorobenzoic acid (m. p. 182°) identical with the compound obtained by Lellmann and Klotz (*Annalen*, **231**, 324) by the oxidation of dichlorotoluene; the *barium* salt of this acid crystallises in short prisms containing $3\frac{1}{2}$ mols. H_2O.

Dichlorobenzonitrile [CN : Cl_2 = 1 : 2 : 6], obtained in like manner, crystallises from alcohol in small, colourless needles, melts at 49°, sublimes readily, and dissolves freely in alcohol, ether, chloroform, and carbon bisulphide, but is more sparingly soluble in glacial acetic acid, light petroleum, and benzene, and insoluble in water. The corresponding *dichlorobenzoic acid* prepared from the nitrile sublimes in colourless needles, melts at 132—133°, and is moderately easily soluble in boiling water, from which it separates in small prisms; its *barium* salt is very readily soluble in water, moderately easily in hot alcohol, and crystallises with $3\frac{1}{2}$ mols. H_2O. This dichlorobenzoic acid is more conveniently prepared from orthochlorotoluene; the last-named compound is first chlorinated, using iron as the halogen carrier, and the mixture of the two isomerides obtained in this way is carefully oxidised with potassium permanganate. The two dichlorobenzoic acids thus produced are partially separated by fractional decomposition of their potassium salts with hydrochloric acid, when the

pure 2:4-dichloro-compound (m. p. 151°) is first precipitated; the later fractions contain both acids, which are separated by the fractional crystallisation of their barium salts. F. S. K.

Nitration and Bromination of Parabromorthotoluic Acid. By A. Claus and L. Beck (*Annalen*, **269**, 207—216; compare Claus and Herbabny, this vol., p. 174).—*Nitrobromorthotoluic acid* [COOH : Me : Br : NO_2 = 1 : 2 : 4 : 5] is obtained, together with a smaller quantity of the isomeride melting at 220°, when finely-divided parabromorthotoluic acid is gradually added to nitric acid of sp. gr. 1·52, heated at about 50°; the two compounds can be separated by means of their magnesium salts. It crystallises in colourless needles, melts at 200°, and sublimes without decomposition, but is not volatile with steam; it is only sparingly soluble in water, but dissolves freely in alcohol, ether, and chloroform. The *potassium* salt, $C_8H_5NO_4BrK + H_2O$, is readily soluble in water and crystallises in lustrous needles. The *sodium* salt crystallises in large nacreous plates with 4 mols. H_2O, and is very readily soluble in water. The *barium* salt crystallises with 4 mols. H_2O in long, lance-shaped needles, and is only moderately easily soluble. The *magnesium* salt forms large, lustrous needles containing 7 mols. H_2O, and is rather more readily soluble than the barium salt.

Nitrobromorthotoluic acid [COOH : Me : NO_2 : Br = 1 : 2 : 3 : 4] crystallises in small, colourless needles, melts at 220°, and is readily soluble in alcohol, ether, and chloroform, but only moderately easily in boiling water; it sublimes unchanged, but is not volatile with steam. The *barium* salt forms nodular aggregates containing 1 mol. H_2O, and is much more readily soluble in water than the corresponding salt of the isomeride just described. The *magnesium* salt is so readily soluble that it does not crystallise from its aqueous solution.

Nitrobromacetotoluidide [NHAc : Me : Br : NO_2 = 1 : 2 : 4 : 6] crystallises in large, colourless, rhombic prisms, and melts at 206°. The corresponding *nitrile*, prepared from nitrobromorthotoluidine by Sandmeyer's method, crystallises from alcohol in broad, yellow needles, melts at 106—107°, and is readily soluble in alcohol and ether, but only very sparingly in hot water; it sublimes in needles, but is only slightly volatile with steam. The corresponding *amide*, $NO_2 \cdot C_6H_2MeBr \cdot CO \cdot NH_2$, is best obtained by heating the nitrile with moderately concentrated sulphuric acid; it crystallises in small, lustrous needles, melts at 235°, and is soluble in alcohol, ether, and boiling water.

Nitrobromorthotoluic acid [COOH : Me : Br : NO_2 = 1 : 2 : 4 : 6], prepared by heating the amide with concentrated hydrochloric acid at 230—250°, crystallises from dilute alcohol in slender needles, melts at 226°, sublimes undecomposed, and is readily soluble in alcohol, ether, light petroleum, and boiling water, but only sparingly in cold water.

Dibromorthotoluic acid [COOH : Me : Br_2 = 1 : 2 : 4 : 5] is formed when parabromorthotoluic acid is heated with bromine and water at 120° for 3 hours; it crystallises in small, lustrous, needles, melts at

210°, and dissolves freely in alcohol, ether, chloroform, and boiling water, but is only sparingly soluble in cold water. The *barium* salt crystallises in needles containing 6 mols. H_2O, and is moderately easily soluble.

Dibromorthotoluonitrile [CN : Me : $Br_2 = 1 : 2 : 4 : 6$], prepared from dibromorthotoluidine, crystallises in colourless, lustrous needles, sublimes without decomposition, and is moderately easily volatile with steam; it melts at 86°, and is soluble in alcohol, ether, chloroform, and boiling water. The corresponding *amide* crystallises in colourless needles and prisms, melts at 198°, and is readily soluble in alcohol, but only sparingly in hot water. The corresponding *acid*

$$[COOH : Me : Br_2 = 1 : 2 : 4 : 6]$$

is formed when the amide is hydrolysed with concentrated hydrochloric acid at 250°; it crystallises in small needles, melts at 157°, and is readily soluble in alcohol, ether, chloroform, and hot water, but only sparingly in cold water. The *barium* salt is readily soluble in water, and crystallises with 1 mol. H_2O. F. S. K.

Amido- and Urethano-tolyloxamic Acids. By H. Schiff and A. Vanni (*Annalen*, **268**, 305—349).—In this paper, the authors give a somewhat fuller account of the experiments which have already been described (Abstr., 1890, 1124; 1891, 702, 833, and 907); there is practically nothing new in the paper except a systematic arrangement of the compounds that have been prepared.

Ethyl amidotolyloxamate, $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot OEt$, can be obtained by heating toluylenediamine with ethyl oxalate, or ethyl oxamate, in concentrated alcoholic solution; it crystallises from hot alcohol in colourless plates, and melts at 168—170°. The *acetyl* derivative, $NHAc \cdot C_6H_3Me \cdot NH \cdot C_2O_2 \cdot OEt$, crystallises from boiling alcohol in colourless plates, melts at 192°, and is almost insoluble in cold alcohol.

Toluyleneoxamide, $C_9H_8N_2O_2$, is formed when ethyl amidotolyloxamate is heated for some time at 180°; it is a yellow substance, melts at 235—260°, and is almost insoluble in all ordinary solvents. F. S. K.

Action of Heat on Salicylic Acid. By C. Graebe and A. Eichengrün (*Annalen*, **269**, 323—325).—When salicylic acid is heated at 195—220°, it is to a great extent converted into phenyl salicylate; if the product is now distilled, a considerable quantity of xanthone is formed.

When parahydroxybenzoic acid (10 grams) is heated in an open vessel at 200°, phenol and carbonic anhydride pass off, and after 18 hours time there remains only a small quantity (0·6 gram) of some compound of high melting point.

Metahydroxybenzoic acid undergoes very little change even on prolonged heating at 210°. F. S. K.

Methyl Salts of Abnormal Structure. By R. Wegscheider (*Monatsh.*, **13**, 252—267).—On methylation, opianic acid can give rise, according to circumstances, to two distinct compounds, which

have the same empirical formula and molecular weight. Of these, one is to be regarded as the true methyl salt; the other, as a pseudo-methyl salt, which, although it behaves in some respects as an ordinary methyl salt, must yet have a dissimilar constitution.

Normal methyl opianate, $COH{\cdot}C_6H_2(OMe)_2{\cdot}COOMe$, is prepared, according to the method previously described by the author (*Monatsh.*, **3**, 356), from silver opianate, methyl iodide, and methyl alcohol, all of which substances must be quite free from acid. It forms crystals, which melt at 82—84°, and, under a reduced pressure of 51—52 mm., boils at 232—234° (uncorr.). This salt can also be obtained from opianyl chloride and methyl alcohol. It is readily hydrolysed on warming with very dilute hydrochloric acid, and is completely volatile in a current of steam.

Pseudo-methyl opianate is formed according to the method of Liebermann and Kleemann (Abstr., 1887, 584), on heating together opianic acid and methyl alcohol, or by saturating a solution of opianic acid in methyl alcohol with sulphurous anhydride, and also, under certain conditions, by the reaction between opianyl chloride and wood spirit. It forms monosymmetric crystals,

$$a : b : c = 0{\cdot}5714 : 1 : 0{\cdot}2792,$$

quite distinct from the crystals of the true methyl salt, from which it is also sharply distinguished by its relatively slight solubility in methyl alcohol. It melts at 103—103·5°, boils at 238—239°, (uncorr.), under a reduced pressure of 51—52 mm., is readily hydrolysed on warming with water, and has, in all probability, the constitution $C_6H_2(OMe)_2{<}\overset{CO\text{———}}{CH(OMe)}{>}$. This accords with the supposition of Liebermann, who states (*Ber.*, **19**, 765 and 2288) that opianic acid is a tautomeric substance, and sometimes reacts as though it had the constitution $C_6H_2(OMe)_2{<}\overset{CO\text{———}}{CH(OH)}{>}O$.

G. T. M.

Bromopianic Acid. By K. Tust (*Ber.*, **25**, 1995—2002).—Bromopianic acid was first prepared by Prinz (Abstr., 1882, 404); the author confirms Wegscheider's value, 204°, for the melting point of the acid. The *calcium* salt is sparingly soluble in hot water, and the *ethyl* salt forms slender, white needles, and melts at 78°. The *trichloride*, $CHCl_2{\cdot}C_6HBr(OMe)_2{\cdot}COCl$, is formed by mixing bromopianic acid and phosphorus pentachloride in the cold and completing the reaction by heating; the product, after well washing with ice water, is dried, dissolved in benzene, and reprecipitated by light petroleum; it crystallises in needles, melts at 100—101°, and is sparingly soluble in water, readily in ether. The *amide*,

$$COH{\cdot}C_6HBr(OMe)_2{\cdot}CO{\cdot}NH_2,$$

formed by dissolving the trichloride in concentrated aqueous ammonia, separates, on cooling, in white needles, and, when recrystallised from water, melts at 180°; it is readily soluble in hot water and alcohol, sparingly so in benzene.

Anilidobromopianic acid, $CH{:}NPh{\cdot}C_6HBr(OMe)_2{\cdot}COOH$, is obtained

by boiling a solution of equal weights of bromopianic acid and aniline in glacial acetic acid (3—4 parts); it melts at 191°, and is insoluble in water and in light petroleum, fairly soluble in hot alcohol, and readily so in hot glacial acetic acid; it is hydrolysed when boiled with concentrated aqueous potash.

Bromopianoximic anhydride, $C_6HBr(OMe)_2<\begin{matrix}CO\\CO\end{matrix}>NH$, is produced when opianic acid and hydroxylamine hydrochloride (equal weights) are heated on the water-bath with 80 per cent. alcohol; the needles which separate from the solution on cooling are collected and recrystallised from benzene; the compound melts at 163—165°, resolidifies above this, and finally melts at 220°; it is readily soluble in hot benzene and chloroform and fairly so in alcohol. By the prolonged boiling of its alcoholic solution, it yields *bromohemipinimide*, $C_6HBr(OMe)_2<\begin{matrix}CO\cdot O\\CH:N\end{matrix}$, which crystallises from benzene in slender, felted needles, melts at 221—222°, and is readily soluble in alcohol, benzene, and chloroform (compare opianoximic anhydride, Liebermann, Abstr., 1887, 46; Perkin, Trans., 1890, 1070).

Bromopianic phenylhydrazide, $C_6HBr(OMe)_2<\begin{matrix}CO\\CH\end{matrix}>N_2Ph$, is prepared by mixing boiling aqueous solutions containing molecular proportions of the acid and phenylhydrazine and boiling for some minutes; it separates on cooling, and, when crystallised from alcohol or benzene, forms stout, white crystals, melts at 160°, and is insoluble in alkalis. Bromopianic acid behaves with phenylhydrazine, therefore, in a manner analogous to opianic acid (see Liebermann, Abstr., 1886, 550). *Bromopianic methylphenylhydrazone*,

$$N_2MePh{:}CH{:}C_6HBr(OMe)_2{\cdot}COOH,$$

is obtained from the acid and asymmetrical methylphenylhydrazine; it crystallises from dilute acetic acid in yellowish-green crystals, melts at 291°, and is insoluble in water, but dissolves in alkalis.

Diphenylhydrazine and hydrazobenzene react with bromopianic acid as with opianic acid (Abstr., 1888, 1209). *Diphenylhydrazonopianic acid*, $N_2Ph_2{:}CH{\cdot}C_6HBr(OMe)_2{\cdot}COOH$, formed by boiling an alcoholic solution of diphenylhydrazine and bromopianic acid (equal mols.), separates from glacial acetic acid in yellow crystals and melts at 230°, whilst *bromopianic hydrazobenzene*, obtained in a similar manner from bromopianic acid and hydrazobenzene, crystallises from benzene in coloured plates, melts at 211°, and is insoluble in alkalis.

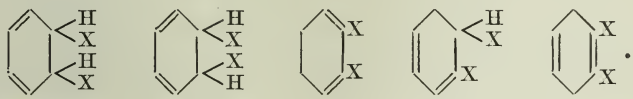
Benzidylbromopianic acid, $C_{32}H_{26}Br_2N_2O_8$, is formed when concentrated aqueous solutions of bromopianic acid (2 mols.) and benzidine (1 mol.) are boiled together; the white needles which separate out are dissolved in ammonia and reprecipitated with acid. The compound does not melt at 300°, and is very sparingly soluble in solvents. It is to be noted that bromopianic acid does not give a condensation derivative with carbamide, as does opianic acid (Abstr., 1888, 1210), whilst its behaviour with orthodiamines has been investigated by Bistrzycki and Cybulski (this vol., p. 1248). Attempts to nitrate

bromopianic acid led to negative results, as the acid is thereby decomposed. A. R. L.

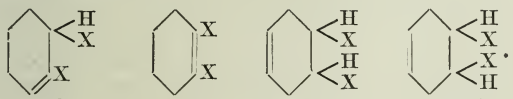
α-Phenylhydrocinnamic Acid. By W. v. Miller and G. Rohde (*Ber.*, **25**, 2017—2020).—The authors have observed that α-phenylhydrocinnamic acid occurs in three modifications which melt respectively at 82°, 88—89°, and 95—96°. α-Phenylhydrocinnamic acid is obtained by reducing α-phenylcinnamic acid (m.p. 172·5°) with 3 per cent. sodium amalgam. When it is dissolved in cold chloroform, and the solution allowed to evaporate slowly, it crystallises in small, colourless prisms which melt at 88—89°. The high melting modification is obtained by heating it at 94° with constant stirring; this modification when cautiously heated melts at 95—96°, but when dissolved in chloroform and allowed to crystallise slowly, it is converted into the low melting modification. The latter melts at 82°, and crystallises in thin plates which are crystallographically distinct from the modification melting at 88—89°. The low melting modification is also obtained by quickly cooling the melted acid. The low melting modification has a sp. gr. = 1·1430, the intermediate modification a sp. gr. = 1·1481, and the high melting modification a sp. gr. = 1·1495. The authors were unable to detect any difference in chemical behaviour between the three modifications.

E. C. R.

Reduction Products of Phthalic Acid. Constitution of Benzene. By A. v. Baeyer (*Annalen*, **269**, 145—206; compare Abstr., 1890, 1275).—The author has prepared four new dihydrophthalic acids, so that the following five isomerides are now known:—



Further investigation has shown that the acid previously described as the Δ³-tetrahydrophthalic acid is the cis Δ⁴-acid, and since no new tetrahydro-acid has been prepared there are at present the following four compounds known:—



Including the two forms of the hexahydro-acid, 11 of the 15 theoretically possible hydrophthalic acids have now been obtained and their constitutions determined; there yet remain to be prepared the cis Δ³- and the trans Δ³-tetrahydro-acids, the Δ²:⁵- and the Δ¹:³-dihydro-acids; it is probable, however, that the first three compounds are either very unstable or incapable of existence. Attempts to prepare the Δ¹:³-acid were unsuccessful.

When phthalic acid is reduced with sodium amalgam in the manner described below, it is converted into the trans $\Delta^{3:5}$-dihydro-acid; the constitution of the reduction product is deduced from the following considerations:—Only two of the theoretically possible dihydro-acids stand in the relation to one another of a fumaroïd to a maleïnoïd acid, namely, the two $\Delta^{3:5}$-compounds; if, therefore, the primary reduction product is a $\Delta^{3:5}$-acid, it must either consist of the two geometrical forms or it must be capable of being converted into a geometrical isomeride. As a matter of fact, the primary reduction product gives an anhydride from which a new, more readily soluble acid is obtained on treatment with water; since this new acid is readily reconverted into the anhydride, and has, moreover, the same chemical properties as the primary reduction product, the latter must be the fumaroïd, the former the maleïnoïd, modification of the $\Delta^{3:5}$-dihydrophthalic acid. These two $\Delta^{3:5}$-dihydrophthalic acids resemble the $\Delta^{2:5}$-dihydroterephthalic acid, the primary reduction product of terephthalic acid, in their behaviour with silver and copper salts (see later). When $\Delta^{2:5}$-dihydroterephthalic acid is warmed with a solution of copper acetate, carbonic anhydride is evolved, and a white precipitate of a cuprous salt is produced; on adding an acid and warming, this precipitate dissolves with separation of cuprous oxide, and the solution then contains benzoic acid and traces of terephthalic acid. The other hydroterephthalic and hydrophthalic acids are not oxidised by copper acetate, and are either not acted on or only slowly oxidised by silver salts.

The reduction of phthalic acid, as is the case with terephthalic acid, takes a different course under different conditions. In acetic acid solution, the trans $\Delta^{3:5}$-dihydro-acid is produced, whereas in alkaline solution, the $\Delta^{2:6}$-dihydro-acid is formed. When reduction takes place in carbonic acid solution, the sole products are sticky, ill-defined acids, probably because under these conditions the carboxyl group also undergoes reduction. When finely-divided phthalic acid is rubbed to a paste with water, the mixture treated with sodium amalgam until solution is complete, and then dilute sulphuric acid added in excess, there is formed a colourless, crystalline precipitate which is insoluble in sodium carbonate but soluble in warm soda; this product melts at 253—255°, and is probably a lactone similar to, or identical with, the compound (hydrodiphthalyl) obtained by Wislicenus (*Ber.*, **17**, 2180) by treating phthalic anhydride with zinc-dust and acetic acid; the solution also contains a considerable quantity of the $\Delta^{3:5}$-dihydrophthalic acid, and has a strong odour of phthalide. This curious difference in behaviour between phthalic acid and its sodium hydrogen salt, on reduction, may possibly be accounted for by assuming, as Anschütz does, that phthalic acid is really the hydrate of the anhydride, but that even in its acid salts it is transformed into the form containing two carboxyl groups.

The author then proceeds to discuss the constitution of the other acids described in the experimental part of the paper; it would, however, be difficult to reproduce his arguments unless they were given in full.

Of the 11 known hydrophthalic acids, all have been converted

into the corresponding anhydride except the trans $\Delta^{3:5}$-dihydro-acid, which gives the anhydride of the cis modification. These anhydrides are all crystalline compounds, and are reconverted into the acids more or less readily by boiling water. The anhydride of the cis modification invariably melts at a lower temperature than that of the trans form, but no other simple relation between melting point and constitution is observable.

The electrical conductivity of eight of the hydrophthalic acids, as determined by Ostwald, is given in the following table:—

Hexahydro-acid (trans)	$K = 0{\cdot}0062$
„ „ (cis)	$K = 0{\cdot}0044$
Tetrahydro-acid, Δ^2	$K = 0{\cdot}0074$
„ „ trans Δ^4	$K = 0{\cdot}0118$
„ „ Δ^1	$K = 0{\cdot}059$
Dihydro-acid, $\Delta^{2:4}$	$K = 0{\cdot}0155$
„ „ $\Delta^{2:6}$	$K = 0{\cdot}0172$
„ „ trans $\Delta^{3:5}$	$K = 0{\cdot}0246$

It will be seen that, just as is the case with the hydronaphthoïc acids (this vol., p. 191), the conductivity of the labile acids is greater than that of the stable forms; speaking generally, the conductivity of the hydrophthalic acids is much lower than that of the alkyl derivatives of succinic acid, although in constitution and in properties the two classes of compounds are in many respects rather closely related.

As regards stability, the hexahydrophthalic acids come first, the dihydro-compounds last, the tetrahydro-acids standing between the two; the trans forms are more stable than the cis isomerides towards alkalis and acids.

The author then discusses at considerable length the behaviour of the hydroterephthalic and hydrophthalic acids on reduction and on oxidation; he shows that it is impossible to draw any conclusions regarding the constitution of benzene from the behaviour of a benzene derivative on reduction, but that it is possible to do so by studying the re-formation of true benzene derivatives from the reduced compounds. The conclusion arrived at is that, with the limitation that para-linkings exist only as long as the benzene nucleus remains intact, Claus' formula is the one which best explains the various reactions of the hydrophthalic and hydroterephthalic acids, and is in fact the only formula which can account for the formation of benzoic acid by the oxidation of the $\Delta^{2:6}$-dihydrophthalic acid. Fresh facts may, however, render it necessary to abandon this view; and in any case the question of the constitution of benzene cannot be considered as settled, because it is impossible as yet to form any representation of what the configuration of the benzene molecule may be; the solution of this problem will be immediately attempted, and in fact experiments on the reduction of isophthalic acid and of carboxy-derivatives of complex benzene derivatives have already been commenced with this object in view.

Although the author claims to have established the existence of a

para-linking in the molecule of phthalic acid, it would not be justifiable, considering the diversity in character of the benzene derivatives, to extend this conclusion generally; in the case of phloroglucinol, for example, it has been proved, with an equal degree of certainty, that the molecule contains three double linkings. It would seem, therefore, that the benzene nucleus exists in two forms, which may be regarded as tautomeric, in the sense that every single derivative has a definite constitution; this view best explains the facts, and gains in probability when it is considered that the ortho- and the para-linking in phenanthrene and anthracene respectively have almost identical properties, and are similar to the "breakable" linkings in the molecule of benzene.

Trans $\Delta^{3:5}$-*dihydrophthalic acid* is formed when 3 per cent. sodium amalgam (400 grams) and 50 per cent. acetic acid (60 c.c.) are added in small portions at a time with constant stirring to a well cooled solution of phthalic acid (20 grams) and sodium acetate (32·8 grams) in water (200 c.c.); when reduction is complete, the solution is mixed with 20 per cent. sulphuric acid (50 c.c.), kept until the separation of sodium sulphate is at an end, the acid then precipitated with 20 per cent. sulphuric acid (150 c.c.), and purified by recrystallisation from boiling water. The yield of the pure acid is 58 per cent. of the phthalic acid employed. It forms long, flat prisms, melts at 210°, is soluble in 610 parts of water at 10°, and in 15—17 parts of boiling water; it is not reduced by sodium amalgam in the cold. The *lead* salt crystallises in short, thick prisms, and is readily soluble in acetic acid. When the acid is boiled for a short time with soda, or for nine hours with water, it is completely converted into the $\Delta^{2:6}$-dihydro-acid. It is more readily oxidised than any of the position isomerides, and at once decolorises potassium permanganate; it immediately reduces ammoniacal silver nitrate solution on warming, and even silver nitrate is reduced after some time. When the acid is warmed with an aqueous solution of copper acetate, there is formed a green precipitate which undergoes decomposition with evolution of carbonic anhydride; if now a little acetic acid is added, and the mixture boiled, cuprous oxide is precipitated and benzoic acid remains in solution. This remarkable reaction is observed even more distinctly when the copper acetate is added drop by drop to a hot solution of the acid; the solution first becomes yellow, carbonic anhydride is evolved, and a white precipitate, probably cuprous benzoate, is produced; on adding acetic acid and heating, the white precipitate is converted into cuprous oxide. If the $\Delta^{2:6}$-dihydro-acid is present in solution, there is formed a colourless, very stable precipitate, which is the cuprous salt of the $\Delta^{2:6}$-acid. Trans $\Delta^{3:5}$-dihydrophthalic acid is decomposed on boiling it with copper sulphate, benzoic acid being formed and carbonic anhydride liberated. It combines directly with 4 atoms of bromine, yielding an oily *tetrabromide* which, on treatment with zinc-dust and acetic acid, is reconverted into the original dihydro-acid; it also combines readily with the halogen acids, giving, with hydrobromic acid, for example, a saturated *dihydrobromide*, which, however, could not be obtained in a crystalline form; this additive product is converted into hexahydro-

phthalic acid on reduction with sodium amalgam, but it does not give an unsaturated acid on treatment with zinc-dust and glacial acetic acid, a fact which shows that the two bromine atoms are not in the ortho-position relatively to one another. When the dihydrobromide is boiled with alcoholic potash, it yields an oil which contains bromine. The reason why the trans $\Delta^{3:5}$-dihydrophthalic acid combines with 4 atoms of bromine, whereas the $\Delta^{2:6}$- and the $\Delta^{2\cdot4}$-dihydro-acids combine with 2 only, is, doubtless, because in the former the pair of double linkings do not join carbon atoms which are directly combined with a carboxyl group, but unite what may be called hydrocarbon groups; if this is really the cause of the great combining power of the acid with the halogens and halogen acids, it is evident that dihydrocymene, or a hydrocarbon of similar constitution, would possess the property in question to an even greater extent.

Cis $\Delta^{3:5}$-*dihydrophthalic acid* is prepared by boiling the trans $\Delta^{3:5}$-modification with acetic anhydride for seven minutes, adding to the cold solution an equal volume of water, and then warming until the decomposition of the anhydride is complete; it is purified by means of its lead salt, which, unlike the salt of the fumaroïd acid, is almost insoluble in acetic acid. It crystallises from hot water in large, flat, colourless prisms, melts at 173—175°, and is soluble in 93 parts of water at 10°. The *anhydride*, prepared by warming the acid with acetic anhydride, crystallises from a mixture of chloroform and ether in colourless needles, melts at 99—100°, and is slowly reconverted into the acid by boiling water. In chemical properties, the cis resembles the trans acid, than which, however, it is rather less stable; it is converted into the $\Delta^{2:6}$-isomeride even by cold 15 per cent. soda, whereas the fumaroïd acid is unchanged under these conditions.

$\Delta^{4:6}$-Dihydrophthalic acid has been previously described (*loc. cit.*), but, at the time, it was suggested that it might be the $\Delta^{2:4}$-acid; it is soluble in 506 parts of water at 10°, and in 322 parts at 25°. On prolonged warming with very concentrated aqueous or alcoholic potash, it is partially converted into the $\Delta^{2:4}$-isomeride. It is only very slowly reduced by sodium amalgam in the cold, but at a higher temperature, and in presence of carbonic acid, it yields the Δ^{2}-, and the two modifications of the Δ^{4}-tetrahydro-acid. On oxidation with potassium permanganate, it yields oxalic acid and phthalic acid, but not succinic acid; when boiled with an alkaline solution of potassium ferricyanide, it gives a large quantity of benzoic acid, this compound being also produced, with evolution of carbonic anhydride, when the acid is treated with freshly precipitated manganese dioxide and dilute sulphuric acid. The *anhydride* is obtained in large, rhombic plates or prisms, when the acid is boiled with acetic chloride for about two hours, and the solution then evaporated over soda-lime and sulphuric acid under reduced pressure; it melts at 83—84°, and dissolves freely in hot water, being reconverted into the original acid. It dissolves in sodium carbonate, yielding an orange-red solution, from which resinous products are precipitated on the addition of an acid; it also resinifies very readily when heated on the water-bath, and at the same time phthalic acid sublimes. When a small quantity of the anhydride is added to very dilute sodium carbonate containing a

little tincture of litmus, the blue colour disappears on shaking, owing to the reduction of the colouring matter, but reappears as soon as the whole of the anhydride has passed into solution.

Dibromotranshexahydrophthalic acid [$Br_2 = 2:6$, $(COOH)_2 = 1:2$], is formed, together with an oily acid, when $\Delta^{2:6}$-dihydrophthalic acid is treated with hydrobromic acid (*loc. cit.*); on treatment with sodium amalgam, it is converted into the transhexahydro-acid. Its *anhydride*, prepared by warming the acid with acetic chloride, crystallises from chloroform in plates, and melts at 157°. When the silver salt of the dibromo-acid is warmed with water, an odour of bromoform is observed, and the mixture turns brown; from the solution, the $\Delta^{2:6}$-dihydro-acid can be isolated.

$\Delta^{2:4}$-*Dihydrophthalic acid* is obtained when the dibromo-acid, just described, is warmed with methyl alcoholic potash (4 mols.) for $1\frac{1}{2}$ hours; it is purified by converting it into the anhydride. It crystallises from warm water in short, concentrically-grouped prisms, melts at 179—180°, and is much more readily soluble in water than the $\Delta^{2:6}$-acid; when a not too concentrated solution of the acid is warmed with copper acetate, there is deposited a colourless, amorphous salt which redissolves on cooling. Its behaviour with oxidising agents is exactly the same as that of the $\Delta^{2:6}$-acid, into which it is converted when boiled with soda. The *anhydride*, prepared by treating the acid with acetic chloride at the ordinary temperature, crystallises from chloroform in colourless cubes, melts at 102—104°, and is readily soluble in warm water, being reconverted into the acid; it dissolves in sodium carbonate, yielding a colourless solution, but it bleaches litmus just like the anhydride of the $\Delta^{2:6}$-acid; when heated, it is converted into the anhydride of the $\Delta^{1:4}$-dihydro-acid. The $\Delta^{2:4}$-acid is the only known dihydrophthalic acid that is reduced by sodium amalgam in the cold.

Dibromotranshexahydrophthalic acid [$Br_2 = 2:4$], prepared by heating the preceding compound with a concentrated, glacial acetic acid solution of hydrogen bromide at 100° for 10 hours, crystallises from ether in rhombic plates, melts at 189—190°, and is very stable towards potassium permanganate; on treatment with sodium amalgam, it is converted into transhexahydrophthalic acid.

Cis Δ^4-*tetrahydrophthalic acid* is obtained when the $\Delta^{2:4}$-dihydro-acid is reduced with sodium amalgam in the cold, in carbonic acid solution; it crystallises from water in well-defined prisms, melts at 174°, and is soluble in 108·1 parts of water at 6°. When boiled with acetic anhydride, it is converted into the *anhydride*, which crystallises from ether in quadratic plates melting at 58—59°. Cis Δ^4-tetrahydrophthalic acid has been previously described (*loc. cit.*) as the Δ^3-tetrahydro-compound, and its formation from the anhydride of the trans Δ^4-tetrahydro-acid was accounted for by assuming that the position of the double linking had shifted; a more exact study has led the author to the conviction that such a shifting does not occur.

$\Delta^{1:4}$-*Dihydrophthalic acid* is obtained by boiling the $\Delta^{2:4}$-acid for six minutes with acetic anhydride, evaporating the solution at the ordinary temperature, and decomposing the purified crystalline an-

hydride prepared in this way with hot water; it separates from cold water in large, flat crystals, melts at 153°, and is partially reconverted into the anhydride when heated at 100°, or when its aqueous solution is concentrated on the water-bath; it is soluble in 59·7 parts of water at 6°. The *anhydride* crystallises in lustrous plates, melts at 134—135°, and sublimes very readily in voluminous, feathery plates. The *lead* salt and the *copper* salt are both sparingly soluble in acetic acid. The *silver* salt is not decomposed by boiling water, and crystallises in concentrically-grouped plates. The acid is not reduced by sodium amalgam, even on warming gently, but it decolorises potassium permanganate almost immediately; on oxidation with dilute sulphuric acid and freshly prepared manganese dioxide, or with a boiling alkaline solution of potassium ferricyanide, it is converted into phthalic acid. When boiled for half an hour with 10 per cent. soda, it is converted into a mixture of the $\Delta^{2:6}$- and the $\Delta^{2:4}$-dihydro-acids. F S. K.

Products of the Action of Nitric Acid on Ethyl Bromotrinitrophenylmalonate. By C. L. Jackson and W. B. Bentley (*Amer. Chem. J.*, **14**, 331—363).—Further slight improvements have been made in the method for producing tribromotrinitrobenzene (Abstr., 1890, 497).

Ethyl bromotrinitrophenylmalonate nitrite,

$$C_6HBr(NO_2)_3{\cdot}C(NO_2)(COOEt)_2,$$

is prepared by warming ethyl bromotrinitrophenylmalonate (*loc. cit.*, 3 grams) with nitric acid of sp. gr. 1·38 (10 grams) for three minutes on the water-bath; the solid which separates on cooling is again warmed with nitric acid, washed with water, dissolved in warm chloroform, and gradually separated from this solution by the addition of an equal volume of alcohol. It crystallises in short, thick, well-formed, lustrous, white prisms; when suddenly heated at 124—126°, it melts to a blood-red liquid which occupies many times the volume of the original solid, and contains gas bubbles. The change can be brought about more slowly at lower temperatures, the final product of the decomposition being ethyl bromotrinitrophenyltartronate (see below). The nitrite is very sparingly soluble in water, more soluble in alcohol, benzene, carbon bisulphide, and glacial acetic acid, and freely soluble in chloroform and acetone. Cold concentrated acids have no action on it, nor have aqueous alkalis, but alcoholic soda turns it red, forming sodium nitrite.

Ethyl anilidotrinitrophenylmalonate nitrite,

$$NHPh{\cdot}C_6H(NO_2)_3{\cdot}C(NO_2)(COOEt)_2,$$

is obtained by mixing ethyl bromotrinitrophenylmalonate with a slight excess of aniline in ether, by which the action is moderated. The liquid is washed with water containing a little hydrochloric acid, evaporated, and the residue recrystallised from chloroform. It forms red rhombohedra, melts at 119°, with slight decomposition, and decomposes violently at 120°. It is insoluble in water and light petroleum; only slightly soluble in alcohol, ether, and carbon bisulph-

ide; more soluble in methyl alcohol and glacial acetic acid, and freely soluble in chloroform, benzene, and acetone. Acids have little or no action on it; alkalis dissolve it pretty freely, showing that it has a distinctly acid bias, supposed by the authors to be due to the influence of the three nitro-groups on the anilido-hydrogen; to confirm this supposition they prepared *sodium anilidotrinitrotoluene*, $NPhNa{\cdot}C_6MeH(NO_2)_3$ (Abstr., 1890, 486), and found it to be a maroon-black powder which is decomposed by water and is soluble in alcohol, but insoluble in ether and benzene.

Ethyl bromotrinitrophenyltartronate,

$$C_6HBr(NO_2)_3{\cdot}C(OH)(COOEt)_2,$$

is formed when the action of nitric acid on ethyl bromotrinitrophenylmalonate is continued on the water-bath for three hours, after which it separates on cooling. It crystallises from alcohol in long, white prisms, melts at 156°, and is insoluble in light petroleum, nearly insoluble in water and carbon bisulphide, soluble in cold alcohol, ether, and chloroform, and freely so in benzene, glacial acetic acid, acetone, and hot alcohol. It shows strong acid tendencies. When mixed with aniline, it yields *ethyl anilidotrinitrophenyltartronate*, $NHPh{\cdot}C_6H(NO_2)_3{\cdot}C(OH)(COOEt)_2$, which exists in a red and a yellow modification. The *red modification* is best obtained by crystallising the crude product several times from alcohol, and then allowing a strong alcoholic solution of these crystals to evaporate slowly at 50—70°; it is thus obtained in well-formed, orange-red prisms, and melts at 143°; it is insoluble in cold water and light petroleum; slightly soluble in hot water, cold benzene, glacial acetic acid, and carbon bisulphide; soluble in cold alcohol, methyl alcohol, ether, and chloroform; freely soluble in hot alcohol, acetone, and hot benzene. From most of its solutions, it crystallises together with the *yellow modification*, which can be obtained pure by dissolving the mixture in warm glacial acetic acid and adding water after some hours. This modification crystallises in slender needles, united into spherical groups; when quickly heated to 122°, it melts and changes into the red modification, into which it is easily converted by slow crystallisation from alcohol; in solubility it resembles the red form, but is generally rather more soluble. Ethyl anilidotrinitrophenyltartronate has well marked acid properties, and the *monopotassium salt*, $NHPh{\cdot}C_6H(NO_2)_3{\cdot}C(OK)(COOEt)_2$, and *disodium salt*,

$$NPhNa{\cdot}C_6H(NO_2)_3{\cdot}C(ONa)(COOEt)_2,$$

were analysed and are described; a solution of the ammonium salt gives the following precipitates:—with a zinc salt, orange-brown; with a manganese salt, brown; with a cadmium salt, reddish-brown; with a copper salt, yellowish-brown; with a lead, mercuric, or silver salt, reddish-brown.

Ethyl anilidotrinitrophenylmalonate,

$$NHPh{\cdot}C_6H(NO_2)_3{\cdot}CH(COOEt)_2,$$

is easily obtained by adding aniline to ethyl bromotrinitrophenylmalonate, and crystallising the product from alcohol. It forms aggre-

gates of long, slender, sharp, yellow needles, and melts at 133°; it is insoluble in light petroleum and cold water, slightly soluble in hot water and carbon bisulphide, freely soluble in hot alcohol, chloroform, benzene, acetone, glacial acetic acid, and ether. It is acid in its behaviour to alkalis, and the solution of its sodium salt gives reddish-brown or yellowish-brown precipitates with most of the dyad metals, the calcium salt being the least, and barium salt the most soluble. Attempts to prepare the above described nitrite by the direct action of nitric acid on this compound failed.

Ethyl trinitrophenylenedimalonate nitrite,

$$CH(COOEt)_2{\cdot}C_6H(NO_2)_3{\cdot}C(NO_2)(COOEt)_2,$$

is prepared from ethyl trinitrophenylenedimalonate (Abstr., 1890, 498) similarly to ethyl bromotrinitrophenylmalonate nitrite. It crystallises in thick, lemon-yellow plates, and melts at 111°. It is insoluble in light petroleum and cold water; slightly soluble in cold alcohol, hot water, and carbon bisulphide; freely soluble in hot alcohol, chloroform, benzene, acetone, glacial acetic acid, and ether. It has acid properties, and a solution of the sodium salt gives yellow precipitates with salts of most of the dyad metals.

Ethyl bromodinitrophenylmalonate nitrite,

$$C_6H_2Br(NO_2)_2{\cdot}C(NO_2)(COOEt)_2,$$

similarly prepared, forms thick, white, rhombic crystals, and melts at 111°. It is nearly insoluble in light petroleum and cold water; soluble in ether, carbon bisulphide, and alcohol, and freely soluble in benzene, chloroform, acetone, and glacial acetic acid. It is decomposed by sodium hydroxide, and is very stable to nitric acid. When it is reduced with hydrochloric acid and tin, *amidohydroxyoxindole chloride*, $NH_3Cl{\cdot}C_6H_3{<}^{CH(OH)}_{NH-CO}{>}$, is obtained; this crystallises in large, yellow plates.

The authors regard the above compounds as nitrites containing the NO_2 group in the side chain attached to the molecule by oxygen and not by nitrogen, first, because of their easy conversion by nitric acid and by heat into the corresponding tartronates, a reaction resembling the conversion of the nitrate of tartaric acid into tartronic acid; and secondly, because the reduction of ethyl bromodinitrophenylmalonate nitrite yields amidohydroxyoxindole chloride, and not diamidoxindole chloride. A. G. B.

Alkyl Salts of Sulphonic Acids. By F. Krafft and A. Roos (*Ber.*, **25**, 2255—2262).—Schiller and Otto have stated that ethyl benzenesulphonate is not formed by the action of ethyl alcohol on benzenesulphonic chloride, but the compound described by them as this salt (this Journal, 1877, i, 463), as also the compounds obtained by Hübner (Abstr., 1884, 1180), were not pure substances. The authors find, however, that methyl and ethyl benzenesulphonate are readily prepared by mixing benzenesulphonic chloride with the alcohol (3 parts), and allowing the mixture to remain for 4—5 days,

pouring the product into ice-cold water, taking up the precipitated oil with ether, and rectifying under diminished pressure.

Methyl benzenesulphonate, $C_6H_5{\cdot}SO_3Me$, is a colourless, almost tasteless oil, d 17°/4° = 1·273, boiling at 150° (15 mm.); whilst ethyl benzenesulphonate resembles it, d 17°/4° = 1·2192, and it boils at 156° (15 mm.). *Propyl benzenesulphonate* is prepared in the same manner, but the reaction requires 12—14 days for completion; it boils at 162—163° (15 mm.), d 17°/4° = 1·1804. Ethyl paratoluenesulphonate melts at 32—33° as stated by Jaworsky (*Zeit. f. Chem.*, 1865, 221), boils at 173° (15 mm.), and has a sp. gr. at 32° = 1·1736.

Methyl parachlorobenzenesulphonate, prepared from *parachlorobenzenesulphonic chloride* (m. p. 53°), melts at 50·5° and boils at 165—166° (15 mm.); whilst the *ethyl* salt melts at 25—26° and boils at 171—172°.

Methyl parabromobenzenesulphonate, prepared from *parabromobenzenesulphonic chloride* (m. p. 75°), melts at 60° and boils at 176° (15 mm.); whilst the *ethyl* salt melts at 39·5° and boils at 181—182° (15 mm.).

Methyl β-naphthalenesulphonate is obtained from *β-naphthalenesulphonic chloride* (m. p. 76—77°); it melts at 53—54° and boils at 224—225° (15 mm.); whilst the ethyl salt melts at 11—12°.

α-Naphthalenesulphonic chloride boils at 194—195° (13 mm.), and yields on treatment with methyl alcohol *methyl α-naphthalenesulphonate*, melting at about 75° and boiling at 214° (15 mm.). The investigation is proceeding. A. R. L.

Phenylhydrindone. By W. v. Miller and G. Rohde (*Ber.*, **25**, 2095—2102).—*Phenylhydrindone*, $C_6H_4{<}\begin{matrix}CH_2\\CO\end{matrix}{>}CHPh$, is prepared by dropping dried pulverised α-phenylcinnamic acid (10 grams) into concentrated sulphuric acid (80 grams) at 140°, shaking, and after a few minutes, pouring the solution on to ice. The resulting milky liquid is shaken with ether, whereby the phenylhydrindone is extracted, and an oil, probably a sulphonic acid, separates in a layer between the aqueous and ethereal solutions. The ethereal solution is washed successively with soda and water, and the phenylhydrindone obtained from it repeatedly crystallised from boiling alcohol, and finally from cold ether, when it is obtained in well-formed white prisms, melts at 77—77·5°, is readily soluble in benzene, alcohol, and ether, sparingly so in light petroleum, and as good as insoluble in water; it distils at 344° with partial decomposition, is volatile with steam, and reduces ammoniacal silver and Fehling's solutions. Phthalic and benzoic acids are formed on oxidation with dilute nitric acid. The *phenylhydrindonehydrazone*, $C_{21}H_{18}N_2$, crystallises from benzene in almost white crystals, which become brownish on exposure to light; it melts at 137—138°, and dissolves in concentrated sulphuric acid with a yellow colour, becoming dark-violet on the addition of ferric chloride.

If an ethereal solution, containing 10 grams of phenylhydrindone, is shaken with seven successive portions of 10 per cent. sodium hydr-

oxide solution (50 grams) for 1—2 hours in each case, and after washing, the ether is distilled off, and the crystalline residue washed with a little ether, *hydroxyphenylhydrindone*, $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CPh\cdot OH$, or $C_6H_4<\begin{matrix}CH(OH)\\CO\text{———}\end{matrix}>CHPh$, is left. On slowly evaporating an ethereal solution, it separates in six-sided tablets, melting at 129°. The corresponding *hydrazone*, $C_{21}H_{18}N_2O$, forms yellow crystals, melts at 160°, and dissolves in concentrated sulphuric acid with a violet colour, becoming blue on the addition of ferric chloride; when, however, its solution in sulphuric acid is placed aside, it becomes claret coloured, and passes into bluish-green on the addition of ferric chloride. The *acetyl* derivative melts at 167°.

β-Deoxybenzoïnorthocarboxylic acid, melting at 169—170°, and identical with that obtained by Gabriel (Abstr., 1885, 1231), separates on acidifying the sodium hydroxide solution, which has been shaken with an ethereal solution of phenylhydrindonephenylhydrazone, as above described.

When phenylhydrindone is oxidised with alkaline potassium permanganate, besides phthalic and benzoic acids, traces of hydroxyphenylhydrindone (m. p. 129°) and other compounds are formed. The investigation is still in progress. A. R. L.

Condensation of the Three Isomeric Methylhydrocinnamic Acids to the Corresponding Methylhydrindones. By Young (*Ber.*, **25**, 2102—2109).—The yield of orthomethylcinnamic acid obtained by Perkin's reaction is poor (see Kröber, Abstr., 1890, 969). Claisen's method (Abstr., 1890, 891), however, gives better results. Orthotolualdehyde (10 grams) is gradually dropped into a well-cooled mixture of sodium (2 grams) in excess of ethyl acetate; after a while the calculated quantity of glacial acetic acid is added to the mixture, which is then diluted with water, and extracted with ether. The acid has the properties already ascribed to it by Kröber (*loc. cit.*).

Orthomethylhydrocinnamic acid is prepared by reducing the last-mentioned acid with sodium amalgam, the solution being kept neutral by means of a current of carbonic anhydride; it is readily soluble in hot water and other ordinary solvents, and separates in elongated, monoclinic prisms.

Orthomethylhydrindone, $C_6H_3Me<\begin{matrix}CO\\CH_2\end{matrix}>CH_2$, is formed when the methylhydrocinnamic acid (10 grams) is dropped into hot concentrated sulphuric acid (15 grams) at a temperature of 180—190°, and the mixture poured on to ice; the hydrindone is driven over in a current of steam, and, subsequently, crystallised from light petroleum, from which it separates in white needles melting at 95°. The *phenylhydrazone*, $C_{10}H_{10}:N_2HPh$, crystallises from dilute alcohol in slender, white needles, melting at 133° with decomposition. When orthomethylhydrindone is oxidised with nitric acid, *methylphthalic acid*, [Me : $(COOH)_2 = 1 : 2 : 3$], melting at 144°, and giving an *anhydride* melting at 109—110°, is formed. The corresponding *methylphthalimide*

is obtained when the acid is treated with ammonium thiocyanate by Aschan's method (Abstr., 1886, 704); it forms nodular groups of needles, and melts at 183—184°.

When meta- or para-methylhydrindone is oxidised with nitric acid, methylphthalic acid [Me : $(COOH)_2 = 1 : 3 : 4$], melting at 124°, is obtained. The methylphthalic acid described by Niementowski (this vol., p. 607) is probably a mixture of two isomerides. A. R. L.

The Formation of Hydrindone Derivatives from Halogen Cinnamic Acids. By W. Miersch (*Ber.*, **25**, 2109—2116; compare Abstr., 1890, 1139).—Orthobromocinnamic acid is prepared by reducing technical orthonitrocinnamic acid by Fischer and Kuzel's method (*Annalen*, **221**, 266), and displacing the amido-group in the product thus obtained by bromine, according to Gattermann's method (Abstr., 1890, 971); it is reduced to the corresponding hydro-acid by hydriodic acid and phosphorus.

Orthobromhydrindone, $C_6H_3Br<\begin{matrix}CO\\CH_2\end{matrix}>CH_2$, is formed by treating orthobromhydrocinnamic acid with concentrated sulphuric acid at 180—190°, the yield being 10 per cent. of the bromo-acid employed; it crystallises from alcohol in colourless needles, and melts at 95·5—96·5°. The *phenylhydrazone* melts at 146—147·5°; whilst parabromhydrindonephenylhydrazone melts at 158—159·5°.

Parachlorhydrocinnamic acid is prepared by reducing paramidocinnamic acid either with sodium amalgam or with hydriodic acid and phosphorus (details being given in the paper), and replacing the NH_2 group by chlorine, by Gattermann's method; it melts at 122°.

Parachlorhydrindone, $C_6H_3Cl<\begin{matrix}CO\\CH_2\end{matrix}>CH_2$, obtained by heating the last-mentioned acid with concentrated sulphuric acid at 180°, melts at 79—80°, and gives a *phenylhydrazone* melting at 136·5—137·5°.

A compound melting at 126—127° was obtained from paraiodohydrocinnamic acid; it is probably paraiodohydrindone.

Meta- and ortho-bromhydrindone, when heated on the water-bath with 25 per cent. nitric acid, give consecutive bromophthalic acid (m. p. 183°); whilst parachlorhydrindone gives, on similar treatment, asymmetrical chlorophthalic acid (m. p. 150—150·5°). A. R. L.

Metadiamidotetramethylbenzidine. By C. Lauth (*Compt. rend.*, **114**, 1208—1211).—Metazodimethylaniline, $N_2(C_6H_4{\cdot}NMe_2)_2$, is obtained in long, orange or red needles, which melt at 118°, by the action of zinc and caustic soda on nitrodimethylaniline in presence of alcohol. It is insoluble in water, but dissolves easily in dilute acids and in about 15 parts of boiling alcohol. It is rapidly attacked by reducing agents. When heated at about 100° with aniline hydrochloride, it yields a blue-violet induline, and with paraphenylenediamine and hydrochloric acid it forms a blue-grey induline.

When reduced with zinc and sodium hydroxide, in presence of alcohol, metazodimethylaniline yields a hydrazo-derivative, which very readily oxidises. To convert this into metadiamidotetramethylbenzidine, the solution is filtered, in an atmosphere of coal-

gas, into boiling hydrochloric acid. It is boiled for 15 minutes, and the base is precipitated with sodium carbonate, and crystallised from alcohol. The azo-derivative may also be reduced by stannous chloride in presence of excess of acid, and the base extracted with benzene.

Metadiamidotetramethylbenzidine forms colourless needles and melts at 165°. It is very soluble in warm benzene or warm alcohol, but is practically insoluble in these liquids when cold; its salts are very soluble in water. With ferric chloride or potassium dichromate, its solutions give an orange coloration; with lead peroxide and acetic acid, a yellow-brown coloration, and with nitrous acid, a beautful violet colour, changing rapidly to brown. Metadiamidotetramethylbenzidine forms no diazo-compounds. With nitrosodimethylaniline, in presence of acetic acid, it yields an azine which imparts a red-violet tint to silk and to cotton mordanted with tannin. It yields no colouring matters with phthalic acid in presence of zinc chloride, or with formaldehyde or benzaldehyde. C. H. B.

Polymethylene Bases from Benzidine and Tolidine. By H. Schiff (*Ber.*, **25**, 1936—1940).—When benzidine is dissolved in an excess of hydrochloric acid, and formaldehyde added to the solution at 70—80°, a red, flocculent precipitate forms after a while; this is collected, and dried between filter-paper. It is a hydrochloride, which gradually loses hydrogen chloride on keeping, the largest amount of chlorine found in the freshly-prepared substance being 19·9 per cent. The free base separates when a dilute solution of the hydrochloride is heated for half an hour with sodium carbonate. It is a yellow powder, insoluble in water and cold alcohol, and only sparingly soluble in boiling alcohol; it decomposes at a high temperature without melting, and formaldehyde distils over when it is boiled with water. It may have one of the two formulæ $OH\cdot CH<\begin{matrix}C_6H_3\cdot N:CH_2\\ |\\ C_6H_3\cdot N:CH_2\end{matrix}$ or $O<\begin{matrix}CH_2\cdot C_6H_3\cdot N:CH_2\\ |\\ CH_2\cdot C_6H_3\cdot N:CH_2\end{matrix}$; the analytical values agree best with the second. Tolidine yields a similar base, $C_{17}H_{16}N_2O$ or $C_{18}H_{18}N_2O$.

When sulphanilic acid is dissolved in an excess of aqueous formaldehyde, by the aid of heat, the solution saturated with barium hydroxide, and the excess precipitated by carbonic anhydride, an amorphous and crystalline barium salt may be separated; the latter is derived from an acid of the composition $C_{15}H_{14}N_2O_6S_2$. A. R. L.

Acridone Derivatives. By M. Schöpff (*Ber.*, **25**, 1980—1984; compare Graebe and Lagodzinski, this vol., p. 1086).—*3-Acridonesulphonic acid*, $C_6H_4<\begin{matrix}NH\\ CO\end{matrix}>C_6H_3\cdot SO_3H$, is obtained by the action of concentrated sulphuric acid on anilidosulphobenzoic acid

$$[NHPh : COOH : SO_3H = 1 : 2 : 4];$$

it dissolves in water and concentrated sulphuric acid, forming a yellow solution having an intensely blue fluorescence; the *barium* salt crystallises with $1\frac{1}{2}$ mols. H_2O. Although the author has not

succeeded in converting xanthone into acridone by the action of ammonia, even at as high a temperature as 260°, he thinks it probable that the carboxy-, hydroxy-, and sulphonic derivatives of xanthone will be found capable of undergoing an analogous change. When anilidoisophthalic acid is distilled under diminished pressure, there is obtained, besides diphenylamine, a small quantity of a compound which is perhaps acridone. The author confirms Graebe and Lagodzinski's statement (*loc. cit.*) that phenylanthranilic acid is obtained on oxidising acetylorthotolylaniline, and he has obtained an acid melting at 152° by the oxidation of diacetylmetahydroxyphenylorthotoluidine. β-Naphthylanthranilic acid is produced by heating together acetylanthranilic acid and β-naphthol for several hours at 200—250°, and, after the whole of the acetic acid has passed over, raising the temperature to 290—295°. The investigation is proceeding.

A. R. L.

Isomeric Change in the Stilbene Series. By J. J. Sudborough (*Ber.*, **25**, 2237—2239).—Zinin has shown (*Annalen*, **149**, 375) that deoxybenzoïn is converted into chlorostilbene when it is treated with phosphoric chloride. The author has prepared methyl-, ethyl-, and benzyl-chlorostilbene from the corresponding alkyldeoxybenzoïns; the products are purified by heating them with dilute alcoholic potash on the water-bath.

Methylchlorostilbene, CMePh:CClPh, is a transparent oil boiling at 316° (corr.), which, when distilled, or boiled in a reflux apparatus, is converted into a solid isomeride melting at 117—118° and boiling at 311° (corr.). Zinin's chlorostilbene is converted in an analogous manner into an isomeride melting at 54°. Benzylchlorostilbene melts at 80°. As to the nature of these isomerides, it is shown that the two methyl derivatives have the same vapour density, so that it is improbable that they are polymerides, but they may be stereoisomerides, or the solid compounds may be phenanthrene derivatives containing 2 atoms of hydrogen less than the liquid ones.

Cetyldeoxybenzoïn, $C_{16}H_{33}$·CHPh·COPh, melts at 76° and boils with partial decomposition at 430°. A. R. L.

Hydroxyketone Dyes. By C. Graebe and A. Eichengrün (*Annalen*, **269**, 295—317; compare Abstr., 1891, 706).—*Sodiotrihydroxybenzophenone*, $C_{13}H_9O_4Na$, prepared by warming trihydroxybenzophenone with sodium carbonate and water, crystallises in yellow needles, and is only sparingly soluble in water. The *potassium* derivative, $C_{13}H_9O_4K$, is a yellow powder. The *lead* derivative, $C_{13}H_8O_4Pb$, is obtained when an ammoniacal solution of trihydroxybenzophenone is treated with lead acetate; it is a yellow powder, insoluble in water. The *triacetyl* derivative, $C_{13}H_7O_4Ac_3$, prepared by boiling the ketone with acetic anhydride, crystallises in colourless plates, melts at 117°, and is soluble in alcohol, glacial acetic acid, and benzene, but insoluble in water, ether, and light petroleum; when heated with phenylhydrazine in alcoholic solution, it is converted into a colourless, crystalline *hydrazone*, $C_{13}H_7O_3Ac_3{:}N_2HPh$, which melts at 130°, and, when treated with hydroxylamine, it yields a yellowish, crystalline *oxime*, $C_{13}H_7O_3Ac_3{:}N{\cdot}OH$, which melts at 135°.

The *methyl* derivative, $C_{13}H_9O_4Me$, is formed as principal product when trihydroxybenzophenone is heated at 100° with potash (3 mols.) and methyl iodide (3 mols.); it separates from alcohol in yellow crystals, melts at 165°, and is readily soluble in chloroform, but more sparingly in alcohol, ether, and glacial acetic acid, and very sparingly in benzene; it is soluble in dilute soda and in alkaline carbonates, yielding yellow solutions. The *dimethyl* derivative, $C_{13}H_8O_4Me_2$, can be obtained by heating sodiotrihydroxybenzophenone with methyl iodide and solid sodium carbonate at 160°; it separates from alcohol in colourless crystals, melts at 131°, and dissolves freely in ether, chloroform, and alkalis, but is only very sparingly soluble in soda, and insoluble in sodium carbonate; when heated with acetic anhydride, it is converted into the *acetyl* derivative, $C_{13}H_7O_4Me_2Ac$, which crystallises from glacial acetic acid in colourless prisms and melts at 98°. The trimethyl derivative could not be obtained.

Nitrotrihydroxybenzophenone, $C_{13}H_9O_4{\cdot}NO_2$, is obtained, together with benzoic acid and a volatile nitro-compound, when trihydroxybenzophenone is carefully warmed with 20 per cent. nitric acid; it separates from hot water in yellowish crystals, melts at 123°, and is soluble in alcohol and ether; it dissolves in alkalis, yielding a yellow solution, and on oxidation with alkaline potassium permanganate it gives benzoic acid. The *dinitro*-compound, $C_{13}H_8O_4(NO_2)_2$, prepared by treating the ketone with nitric acid of sp. gr. 1·4 at the ordinary temperature, is a yellow substance, melts at 133° with decomposition, and dissolves in water, alcohol, and alkalis, yielding yellow solutions. The *trinitro*-compound, $C_{13}H_7O_4(NO_2)_3$, melts at 118°, and is only sparingly soluble in water, but readily in alcohol.

Bromotrihydroxybenzophenone, $C_{13}H_9O_4Br$, is formed when the ketone is treated with bromine in alcoholic glacial acetic acid solution; it crystallises from alcohol in lemon-yellow prisms, melts at 149°, and is moderately easily soluble in alcohol, ether, and glacial acetic acid, but only sparingly in benzene; on oxidation with potassium permanganate, it yields benzoic acid, and, when treated with nitric acid, it is converted into the mononitro-compound described above.

Tetrahydroxybenzophenone, $C_{13}H_{10}O_5 + H_2O$ (*loc. cit.*), crystallises in greenish-yellow plates, sublimes in nearly colourless needles, and is readily soluble in alcohol, ether, and glacial acetic acid, but only sparingly in water, benzene, and light petroleum; it loses its water at 100°, the anhydrous substance melting at 149°. It dissolves in potash, yielding a yellowish-red solution which rapidly turns dark green on exposure to the air, with separation of a dark precipitate; it is also soluble in sodium carbonate and in ammonia, but is reprecipitated by carbonic acid. In solutions of the sodium or ammonium derivative, aluminium salts produce a golden-yellow, lead and magnesium salts a reddish-yellow, calcium chloride a greenish-yellow, and ferric chloride a yellowish-brown, precipitate. The *sodium* derivative, $C_{13}H_9O_5Na + H_2O$, is quickly deposited in yellow crystals when the ketone is suspended in hot water and treated with sodium carbonate; it is rather sparingly soluble in water. The *tetracetyl* derivative, $C_{13}H_6O_5Ac_4$, crystallises from alcohol and acetic acid in colourless scales, melts at 118°, and combines with phenylhydrazine to form a

colourless, crystalline *hydrazone*, which melts at 129°. The *bromo*-derivative, $C_{13}H_9BrO_5$, is formed when tetrahydroxybenzophenone is treated with bromine in cold glacial acetic acid solution; it crystallises from dilute alcohol in yellow prisms, melts at 200°, and dissolves in sodium carbonate and in dilute potash with a yellow coloration.

Bromodihydroxyxanthone, $C_{13}H_7BrO_4$, is obtained when bromine is added to a glacial acetic acid solution of tetrahydroxybenzophenone and the mixture heated to boiling; it crystallises from alcohol in almost colourless needles, and turns brown at 310°, but does not melt at 360°; it dissolves in potash with a blood-red coloration.

Tribromodihydroxyxanthone, $C_{13}H_5Br_3O_4$, can be prepared by boiling tetrahydroxybenzophenone with a large excess of bromine in glacial acetic acid solution; it is an almost colourless compound, does not melt at 360°, and dissolves in potash, yielding a deep-red solution.

Hydroxynaphthyl trihydroxyphenyl ketone, $OH\cdot C_{10}H_6\cdot CO\cdot C_6H_2(OH)_3 + H_2O$, is formed when gallic acid is heated with α-naphthol and zinc chloride; it crystallises from alcohol in greenish-yellow prisms or needles, loses its water at 100°, melts at 246°, and is only moderately easily soluble in alcohol and glacial acetic acid, and insoluble in water, benzene, and light petroleum; it dissolves in concentrated sulphuric acid with a deep-red, and in alkalis with a yellowish-red, coloration. The *potassium* derivative, $C_{17}H_{11}O_5K$, is a brown powder. The *sodium* derivative, $C_{17}H_{11}O_5Na$, crystallises in brown needles, and is only sparingly soluble in water. The *hydrazone*, $C_{17}H_{12}O_4{:}N_2HPh$, crystallises from alcohol in yellowish-brown plates, melts at 210° with decomposition, and is soluble in ether and glacial acetic acid, but insoluble in benzene. The *tetracetyl* derivative, $C_{17}H_8O_5Ac_4$, forms yellow crystals, melts at 129°, and is readily soluble in alcohol, benzene, and glacial acetic acid, but only sparingly in ether. When the ketone is heated with sulphuric acid, it is decomposed into naphthol and gallic acid; it is completely decomposed by warm concentrated nitric acid.

A bromo-derivative of the composition $C_{34}H_{16}O_9Br_6$ is formed when hydroxynaphthyl trihydroxyphenyl ketone is treated with excess of bromine in glacial acetic acid solution at the ordinary temperature; it separates from alcohol in crystals, melts at 293°, and is moderately easily soluble in alcohol, glacial acetic acid, and ether, but almost insoluble in benzene and light petroleum. When bromine is gradually added to an alcoholic solution of the ketone until a permanent coloration is produced, a considerable development of heat occurs, and, on cooling, a yellow, crystalline compound, which melts at 246° and has probably the composition $C_{17}H_7Br_3O_4$, is deposited.

A *dinitro*-compound of the composition $C_{17}H_{10}O_5(NO_2)_2$ is formed when hydroxynaphthyl trihydroxyphenyl ketone is heated at 40—50° with dilute nitric acid; it crystallises from alcohol in yellow needles, melts at 134° with decomposition, and is soluble in potash.

F. S. K.

Behaviour of Aromatic Hydroxyketones with Sulphuric Acid and with Ammonia. By C. Graebe and A. Eichengrün (*Annalen*, **269**, 318—323; compare preceding abstract).—When the hydroxy-derivatives of benzophenone are treated with sulphuric acid

under suitable conditions, they are decomposed, and the more readily the greater the number of hydroxy-groups in the molecule; that part of the molecule which is combined with the smaller number of hydroxyl groups is converted into an acid, whilst the remainder is transformed into a phenol or phenolsulphonic acid. Hydroxybenzophenones, such as orthodihydroxybenzophenone, which are readily converted into xanthone derivatives form exceptions to the above rule.

Hydroxyamidobenzophenone, $OH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NH_2$, is formed when orthodihydroxybenzophenone is boiled with dilute ammonia, but the yield is better when the ketone is treated with excess of alcoholic ammonia at the ordinary temperature. It is a yellow, crystalline compound, melts at 222°, and is soluble in hot alcohol, chloroform, and ethyl acetate, but only sparingly in ether and benzene; it dissolves in cold alkalis, and in warm alkaline carbonates with a yellow, and in concentrated sulphuric acid with a red, coloration, but its solutions in dilute acids are colourless. The *hydrochloride* crystallises from dilute alcohol in colourless prisms, and melts at 242°; when this salt, or the base itself, is submitted to dry distillation, it is converted into xanthone with liberation of ammonia.

When tetrahydroxybenzophenone (m. p. 149°) is heated with dilute ammonia at 150°, it is converted into the corresponding dihydroxyxanthone (compare Abstr., 1891, 706); paradihydroxybenzophenone and orthoparadihydroxybenzophenone, on the other hand, are not acted on by ammonia. Salicylresorcinol is readily decomposed by ammonia at the ordinary temperature, yielding salicylamide and resorcinol. F. S. K

Derivatives of Deoxybenzoïn. By P. Petrenko-Kritschenko (*Ber.*, **25**, 2239—2242).—Parachlorodeoxybenzoïn is prepared from paranitrophenylacetic acid (prepared from benzoyl cyanide) by reducing it, and converting the amido-acid thus formed into the chloro-acid by Sandmeyer's method; the latter is then dissolved in chloroform, the solution heated with phosphorus pentachloride, and the non-volatile residue, left on distilling the product under diminished pressure, is dissolved in benzene, and heated on the water-bath with a small quantity of aluminium chloride. The parachlorodeoxybenzoïn, when crystallised from alcohol, melts at 133°. When it is dissolved in sodium ethoxide solution, benzyl chloride (2 mols.) added, and the mixture heated for about 12 hours, the *benzyl* derivative, $C_6H_4Cl\cdot CH(CH_2Ph)\cdot COPh$, melting at 138°, is obtained.

Parachlorodesaurin, $C_6H_4Cl\cdot C(CS)\cdot COPh$, is formed by heating parachlorodeoxybenzoïn with potassium hydroxide in fine powder (2 parts) and carbon bisulphide (20—30 parts) on the water-bath. It separates from xylene as a bright-yellow, microcrystalline mass, and melts at 280°.

Paranitrodeoxybenzoïn, prepared from paranitrophenylacetic chloride by the Friedel-Craft reaction, melts at 145°, and is, perhaps, identical with the compound Golubeff obtained by nitrating deoxybenzoïn (Abstr., 1879, 150 and 790). Experiments are now in progress on the action of benzyl chloride on the nitro-compound. A. R. L.

The Fluoresceïn Group. By R. Meyer and H. Hoffmeyer (*Ber.*, **25**, 2118—2121).—The formula ascribed by the authors in a former paper (this vol., p. 970) to fluoran was not experimentally established.

Hydrofluoranic acid, which has been obtained both by v. Baeyer and by the authors by reducing fluoran, and which may be represented by the formula $COOH\cdot C_6H_4\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O$, was distilled with lime (3 parts), xanthone being isolated. The latter is also formed, together with benzene, when fluoran is distilled with lime (4 parts); these facts prove, therefore, the accuracy of the formulæ assigned to fluoran and fluoresceïn (*loc. cit.*), as also that given above to hydrofluoranic acid.

When hydrofluoranic acid is distilled with baryta or soda-lime, or when fluoran is distilled with soda-lime and zinc-dust, a compound is obtained crystallising in white needles and melting at 143°. It is being further investigated. A. R. L.

Condensation of Cinnamic Acid with Hydrocarbons. By C. Liebermann and A. Hartmann (*Ber.*, **25**, 2124—2131).—When cinnamic acid (25 grams) is mixed with benzene (50 grams) and concentrated sulphuric acid (125 grams), and the mixture heated on the water-bath for 1—2 hours, then poured into water and extracted with ether, the aqueous acid liquid is found to contain sulphonic acids, which give diphenylpropionic acid on heating them with hydrochloric acid at 220°. The ethereal solution is distilled, and the residue extracted with sodium carbonate solution, when phenylhydrindone (see below) remains, whilst diphenylpropionic acid and a smaller quantity of phenylenediphenyldipropionic acid pass into solution. The two acids are subsequently separated by means of the difference in their solubility in ether, the former being more readily soluble in that solvent than the latter. To obtain the maximum yield of diphenylpropionic acid, the above quantity of sulphuric acid is diluted with 10 per cent. of water.

When the diphenylpropionic acid (*loc. cit.*) is dissolved in alkali carbonate, a 5 per cent. solution of potassium permanganate dropped in, and, simultaneously, a current of steam passed through the mixture, benzophenone is driven over.

Phenylenediphenyldipropionic acid, $C_6H_4(CHPh\cdot CH_2\cdot COOH)_2$, crystallises from alcohol in small, white needles, and melts at 235°; the *barium* salt crystallises with $7H_2O$. The acid owes its origin to the condensation of diphenylpropionic acid with cinnamic acid.

Phenylhydrindone, $C_6H_4<\begin{matrix}CHPh\\CO\end{matrix}>CH_2$, forms colourless, lustrous needles, dissolves readily in alcohol, ether, benzene, and glacial acetic acid, and melts at 78°; the *oxime* melts at 141°, and the *hydrazone* melts at 130° (compare v. Miller and Rohde, this vol., p. 1220).

When v. Pechmann's β-phenylumbelliferone (Abstr., 1884, 67) is dissolved in alcohol, and allowed to remain for two days with an excess of sodium amalgam at 50—60°, phenylhydroxyhydrocoumarin (m. p. 137°), identical with that prepared by the condensation of cinnamic acid and resorcinol, is obtained. A. R. L.

Nitro-β-naphthols. By F. Gaess (*J. pr. Chem.* [2], **45**, 614—616). —1′ : 2′-*Nitronaphthol* is prepared by heating 1′ : 2′-nitronaphthol ethyl ether (Abstr., 1891, 459) in 15 parts of a mixture of glacial acetic acid (10 parts) and strong hydrochloric acid (5 parts) for 6—8 hours at 160—170°; the solution is poured into water, the acid nearly neutralised, and the precipitated naphthol filtered off, and purified by solution in ammonia and reprecipitation by hydrochloric acid. It crystallises from hot water in golden needles, melts at 144—145°, and dissolves easily in alcohol, ether, chloroform, acetone, and benzene; it has feebly acid properties, and forms unstable salts. The *acetyl* derivative crystallises from aqueous alcohol in long, pale-yellow needles, melts at 101—102°, and dissolves easily in alcohol and ether, but more sparingly in water.

2 : 2′-Nitronaphthol ethyl ether is not so easily decomposed. By using a mixture of 15 parts of hydrogen chloride and 85 parts of glacial acetic acid, and heating at 200—210°, both 2 : 2′-nitronaphthol and chloro-2 : 2′nitronaphthol are produced; they may be separated by crystallisation from aqueous alcohol or aqueous acetic acid, in both of which the chloro-derivative is less soluble. 2 : 2′-*Nitronaphthol* forms yellow needles, and melts at 156—158°; the *acetyl* derivative crystallises in colourless needles, and melts at 151—152°. *Chloro*-2 : 2′-*nitronaphthol* crystallises in yellow needles, and melts at 192°. A. G. B.

Nitro-β-naphthaquinone. By T. Zincke (*Annalen*, **268**, 257—260).—The author and his pupils have studied the action of chlorine on nitro-β-naphthaquinone; the results of the investigation are given in the following abstracts. F. S. K.

Action of Chlorine on Nitro-β-naphthaquinone in Glacial Acetic Acid Solution. By T. Zincke and M. Latten (*Annalen*, **268**, 260—297).—*Orthodichloronitrethylbenzoylcarboxylic acid*,

$$OH\cdot NO{:}CCl\cdot CHCl\cdot C_6H_4\cdot CO\cdot COOH,$$

is obtained, together with an oily bye-product, when a rapid stream of dry chlorine is passed into glacial acetic acid containing finely-divided nitro-β-naphthaquinone in suspension, the saturated solution kept for 24 hours, then filtered, and evaporated at the ordinary temperature; on keeping, the acid is gradually deposited in crystals and is separated from the yellow mother liquors by filtration. It separates from glacial acetic acid in large, lustrous, seemingly monoclinic crystals, and from hot benzene in colourless needles or prisms, turns yellow at 163—165°, and melts at 174° with effervescence; it dissolves freely in alcohol, ether, and glacial acetic acid, but is only sparingly soluble in benzene, and almost insoluble in light petroleum. It is soluble in cold water, but is reprecipitated from the solution on the addition of hydrochloric acid; it is quickly decomposed by hot water and by carbonates. It dissolves in ammonia and in an alcoholic solution of hydroxylamine yielding beautiful, blue solutions, from which a dark-blue, amorphous substance is precipitated either immediately or on the addition of an acid; when warmed with stannous chloride

and hydrochloric acid, it is decomposed, with liberation of carbonic anhydride and ammonia; it crystallises unchanged from concentrated nitric acid, but on oxidation with chromic acid it yields a lactone of the composition $C_9H_6ClNO_4$ (see later). When the acid is heated at 105—110°, it loses 1 mol. H_2O; the anhydride obtained in this way takes up water very readily, and is reconverted into the acid on recrystallisation even from dry solvents. An *acetyl* derivative, $C_{10}H_6Cl_2NO_5Ac$, is formed when the acid is heated at 100° with acetic chloride; it crystallises from benzene in transparent, quadratic, efflorescent plates, melts at 154°, and is insoluble in alkalis; it is decomposed by warm dilute soda, yielding a dirty, flocculent substance. The *methyl* salt, $C_{11}H_9Cl_2NO_5$, prepared by treating the acid with methyl alcohol and sulphuric acid, crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 139°, and is soluble in ether, benzene, and soda, but insoluble in sodium carbonate; its *acetyl* derivative, $C_{11}H_8Cl_2NO_5Ac$, crystallises from methyl alcohol in transparent plates, and melts at 130—131°.

A *lactone* of the composition $C_{10}H_6ClNO_5$ is formed when the ketonic acid is treated with 10 per cent. sodium carbonate solution; it crystallises from hot benzene in slender, colourless needles, melts at 139°, and is only sparingly soluble in ether, but moderately easily in alcohol and glacial acetic acid; it frequently decomposes on keeping, especially when impure, with evolution of ruddy fumes, and it is readily oxidised to phthalic acid on treatment with nitric acid. Chromic acid converts it into a lactone of the composition $C_9H_6ClNO_4$ (see below) with liberation of carbonic anhydride, but acetic chloride is without action; its behaviour with stannous chloride, ammonia, and hydroxylamine is the same as that of the ketonic acid. It is not acted on by chlorine in glacial acetic acid solution, but on treatment with calcium hypochlorite it is converted into dichloronitromethylphthalide; its constitution is probably represented by the formula

$$CO<\begin{matrix}CO\cdot O\\ C_6H_4\end{matrix}>CH\cdot CCl{:}NO\cdot OH.$$

When the lactone just described is dissolved in water and the acid solution extracted with ether, a syrupy hydroxy-acid is obtained; this is not reconverted into the lactone on warming, and forms no well-characterised salts; its *acetyl* derivative is insoluble in water, but soluble in alkaline carbonates, a fact which indicates the presence of two hydroxyl groups in the molecule of the acid. The *dimethyl* derivative, $C_{12}H_{12}ClNO_6$, prepared by treating the hydroxy-acid with methyl alcohol and sulphuric acid, separates from methyl alcohol in lustrous, well-defined crystals, melts at 125—131°, and is insoluble in sodium carbonate. The constitution of the hydroxy-acid could not be determined, but it is evidently not expresesd by the formula $NO_2\cdot CHCl\cdot CH(OH)\cdot C_6H_4\cdot CO\cdot COOH$.

The *lactone* of orthochloronitrohydroxyethylbenzoic acid,

$$\begin{matrix}CO\cdot O\\ |\\ C_6H_4\end{matrix}>CH\cdot CCl{:}NO\cdot OH,$$

is formed when the ketonic acid described above is dissolved in sodium

carbonate, the solution acidified with glacial acetic acid, and then warmed with excess of chromic acid; it crystallises in colourless needles or plates, melts at 127° with previous softening, and is readily soluble in alcohol, glacial acetic acid, and benzene, but more sparingly in ether and light petroleum; it dissolves in sodium carbonate and in soda, but is reprecipitated on the addition of an acid. It is decomposed by stannous chloride with liberation of ammonia, but it is not acted on by aniline and hydroxylamine.

Orthochloronitromethoxyethylbenzoic acid,

$$OH{\cdot}NO{:}CCl{\cdot}CH(OMe){\cdot}C_6H_4{\cdot}COOH,$$

is formed when the preceding compound is treated with ice-cold methyl alcoholic potash, and the solution then poured into excess of cold hydrochloric acid. It crystallises from benzene in lustrous, quadratic plates, melts at 171° with decomposition, and dissolves freely in alcohol, glacial acetic acid, ether, and sodium carbonate. The *methyl* salt $C_{11}H_{12}ClNO_5$ crystallises from methyl alcohol in lustrous, colourless needles melting at 111°. When the methoxy-acid is treated with chlorine in sodium carbonate solution, it is converted into a compound of the constitution

$$NO_2{\cdot}CCl_2{\cdot}CH(OMe){\cdot}C_6H_4{\cdot}COOH;$$

this substance crystallises from benzene in lustrous prisms, and melts at 189°.

Nitromethylenephthalyl, $\begin{matrix}CO{\cdot}O\\ |\\ C_6H_4\text{-}\end{matrix}\!>\!C{:}CH{\cdot}NO_2$, is obtained by oxidising the bye-product formed in the preparation of chloronitrethylbenzoylcarboxylic acid. The mother liquors from the crystalline acid (see above) are diluted with acetic acid, the mixture warmed with sodium acetate, then strongly acidified with hydrochloric acid, and the heating continued until only a slight turbidity is produced on the addition of water; the dilute solution is then filtered from resinous products, boiled with excess of chromic acid, and the precipitate repeatedly treated with hot alcohol, which extracts the lactone of orthochloronitrohydroxyethylbenzoic acid. The nitromethylenephthalyl remains undissolved and is purified by recrystallisation from hot glacial acetic acid, from which it separates in yellowish needles or plates melting at 194°. It is only sparingly soluble in alcohol, ether, and benzene, is decomposed by hot soda, and is not acted on by chlorine in glacial acetic acid solution; on treatment with stannous chloride, it is decomposed with liberation of ammonia.

When nitromethylenephthalyl is dissolved in ice-cold methyl alcoholic potash, and the solution acidified with cold, dilute hydrochloric acid, a compound of the composition $C_{10}H_{10}O_4$ is obtained; this substance crystallises from a mixture of benzene and light petroleum in long, dirty-white needles, melts at 147°, and is probably *methoxyacetophenonecarboxylic acid*, $OMe{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$.

Dichloronitromethylphthalide, $\begin{matrix}CO{\cdot}O\\ |\\ C_6H_4\text{-}\end{matrix}\!>\!CH{\cdot}CCl_2{\cdot}NO_2$, the lactone of orthodichloronitrohydroxyethylbenzoic acid, is formed, with evolution

of carbonic anhydride, when a glacial acetic acid solution of nitro-β-naphthaquinone, which has been saturated with chlorine, is poured into a large volume of cold water; it can also be prepared by treating either the lactone melting at 139°, or the lactone melting at 127°, already described, with a concentrated solution of calcium hypochlorite. It crystallises in colourless, lustrous needles, melts at 94°, and is readily soluble in alcohol, glacial acetic acid, benzene, and chloroform, but more sparingly in light petroleum; it is very stable and is not acted on by aniline, hydroxylamine, acetic chloride, or concentrated nitric acid, but when warmed with stannous chloride it is decomposed with liberation of ammonia; it is quickly decomposed by warm concentrated sulphuric acid, yielding phthalic acid. When heated with potassium acetate in alcoholic solution, it is converted into dichloromethylenephthalyl (m. p. 129°), identical with the compound previously described by Zincke and Cooksey (Abstr., 1890, 786). F. S. K.

Action of Chlorine on Nitro-β-naphthaquinone in Chloroform Solution. By T. Zincke and O. Scharfenberg (*Annalen*, **268**, 297—305).—*Dichloronitro-αβ-diketohydronaphthalene hydrate*,

$$C_6H_4<\begin{matrix}CO\cdot CO\\CHCl-\end{matrix}>CCl\cdot NO_2 + H_2O,$$

is obtained as sole product when nitro-β-naphthaquinone is treated with chlorine in chloroform solution in absence of water. It crystallises from a mixture of benzene and light petroleum in almost colourless needles, melts at 115—116° with decomposition, and dissolves freely in benzene, chloroform, and ether, but is only sparingly soluble in light petroleum. It does not lose its water over sulphuric acid under reduced pressure, but when heated at 100—105° it is partially converted into dichloronitrethylbenzoylcarboxylic acid (see preceding abstract); this acid is also formed when the hydrate is dissolved in glacial acetic acid, anhydrous ether, or benzene. It dissolves in sodium carbonate, and, on acidifying the solution, the lactone (m. p. 139°) already described is precipitated. When treated with methyl alcohol, it is converted into the methyl salt of dichloronitrethylbenzoylcarboxylic acid, and when heated for a short time with acetic chloride at 100° it is transformed into dichloro-β-naphthaquinone (m. p. 183°); with stannous chloride in glacial acetic acid solution, it yields nitro-β-naphthaquinone.

When finely-divided nitro-β-naphthaquinone is treated with a concentrated solution of calcium hypochlorite, it is quickly converted into dichloronitromethylphthalide. F. S. K.

Nitration of β-Naphthylamine. By P. Friedländer and S. Szymanski (*Ber.*, **25**, 2076—2083).—The authors have obtained the 2 : 4′- and 2 : 1′-nitronaphthylamines by treating β-naphthylamine nitrate with concentrated sulphuric acid.

β-Naphthylamine nitrate, dried at 100° and in a fine state of division, is gradually added to 10 times the quantity of well-cooled, concentrated sulphuric acid. The temperature is kept below 5° by

means of a freezing mixture. When the nitrate is dissolved, the mixture is poured into 6—8 times the quantity of water, and the hot solution separated from the resin which is formed. On cooling, the sulphates of the nitro-compounds separate as a brownish-yellow, crystalline mass. The nitro-bases are obtained from the sulphates by treatment with ammonia, and are fractionally crystallised from benzene or alcohol. The less soluble 2 : 4′-nitro-β-naphthylamine is thus easily obtained pure. The 2 : 1′-compound is obtained by acetylating the mixed bases with acetic anhydride, crystallising the acetyl compound from alcohol, with the addition of animal charcoal, until it melts at 195·5°, hydrolysing with dilute sulphuric acid (1 : 1), and finally treating the sulphate with ammonia.

2 : 4′-*Nitro-β naphthylamine* crystallises in beautiful, red, lustrous needles, melts at 143·5°, and is easily soluble in hot alcohol, benzene, and acetic acid, more sparingly in hot water, and insoluble in cold water and light petroleum. The *hydrochloride* is easily soluble in hot water, and crystallises in colourless needles. The *sulphate* is sparingly soluble, and crystallises in yellowish-white leaflets. Both salts partially decompose when warmed with a large quantity of water or alcohol. The *acetyl compound* crystallises from alcohol in thick, yellowish-brown rhombs, and from benzene in yellow, radiating needles, melts at 185·5°, and is easily soluble in alcohol and acetic acid, sparingly so in benzene. The *benzoyl compound* crystallises in needles, and melts at 181·5°.

2 : 4′-*Nitro-β-naphthol* is obtained by diazotising the preceding amido-compound and heating the dilute solution of the diazo-compound, acidified with sulphuric acid, with the addition of a small quantity of carbamide as long as nitrogen is evolved. It crystallises from water in bright, yellow needles, melts at 147°, and is sparingly soluble in cold water, easily so in hot water, in the other usual solvents, and in alkalis. The salts are easily soluble in water, with a bright, yellowish-red coloration. The *ethyl salt*, obtained by boiling an alcoholic solution of the potassium salt with ethyl iodide, crystallises from alcohol in yellow needles, and melts at 115°.

2 : 4′-*Amido-β-naphthol* was not obtained pure on account of the ease with which it oxidises on exposure to air. By cautiously reducing the nitronaphthol with excess of stannous chloride, the stannochloride of the amidonaphthol is obtained in white needles which are completely converted into the hydrochloride when crystallised from concentrated hydrochloric acid. The amidonaphthol is obtained by decomposing the hydrochloride with sodium hydrogen carbonate. It forms a white, crystalline mass, and is easily soluble in the ordinary solvents, alkalis, and acids. The aqueous and alcoholic solutions have a beautiful, violet-blue fluorescence.

2 : 4′-*Naphthylenediamine* is obtained by reducing the above nitro-β-naphthylamine with iron filings and acetic acid. The product is boiled out with water, converted into sulphate, and the sulphate purified by crystallisation from water. The free base is obtained by decomposing the sulphate with sodium hydroxide. It crystallises in short, white needles, melts at 77·5°, is easily soluble in hot water, alcohol, benzene, and acetic acid, less so in cold water and ether, and

darkens on exposure to air. The aqueous solution has a strong, blue fluorescence, and gives a violet-brown coloration with ferric chloride or calcium chloride. The *hydrochloride* is easily soluble in water, sparingly so in hydrochloric acid. The *sulphate* forms sparingly soluble, white needles which turn violet on exposure to the air. The *diacetyl compound* crystallises in colourless needles, melts at 257°, and is sparingly soluble in alcohol. When the diamine is treated with the calculated quantity of nitrite in strongly acid solution, it is easily converted into a tetrazo-compound which yields brownish-violet dyes with naphtholsulphonic acids. These dyes, however, have scarcely any affinity for unmordanted cotton.

2 : 4′-Dichloronaphthalene is obtained from the preceding diamine by converting it into the tetrazo-compound and decomposing the latter with copper-dust and hydrochloric acid. It melts at 48°, and has all the properties assigned to it by Erdmann and Kirchhoff.

2 : 1′-*Nitro-β-naphthylamine* crystallises in beautiful, red, lustrous needles, melts at 103·5°, is easily soluble in most solvents, sparingly so in hot water, and insoluble in light petroleum. The *sulphate* and *hydrochloride* are somewhat less soluble than the salts of the 2 : 4′-compound, and are partially decomposed when heated with water or alcohol. The *acetyl compound* crystallises in long, yellow needles, melts at 195·5°, and is sparingly soluble in benzene and alcohol, more easily so in acetic acid. The *benzoyl compound* crystallises from alcohol in greenish-yellow needles, and melts at 162°.

2 : 1′-*Nitro-β-naphthol* crystallises from dilute alcohol in long, deep-yellow needles, melts at 142°, and is easily soluble in most solvents, sparingly so in water. It yields salts with the alkalis and alkaline earths which dissolve with a deep, dark-red coloration.

2 : 1′-*Amido-β-naphthol* crystallises from ether in small, white needles which darken on exposure to air, blackens at 180°, decomposes at 212—218° without melting, and is easily soluble in alkalis, acids, water, alcohol, and ether.

2 : 1′-*Naphthylenediamine* crystallises from benzene in white leaflets, from water in feathery needles, melts at 117·5°, darkens on exposure to air, and is easily soluble in acetic acid, alcohol, and benzene, less so in water, and very sparingly so in ether and light petroleum. With ferric chloride, the aqueous solution gives a beautiful violet coloration. The *sulphate* and *hydrochloride* are easily soluble in water. The *diacetyl derivative* crystallises from alcohol in small rhombohedra, and melts at 213°. The 2 : 1′-diamine yields brownish-violet disazo-dyes similar to those from the 2 : 4′-compound. The 2 : 1′-dichloronaphthalene obtained from it melts at 61°.

E. C. R.

Natural Synthesis of the Vegetable Hydrocarbons. By Maquenne (*Compt. rend.*, **114**, 677—680).—Whilst it is easy to trace the connection between the carbohydrates, the fatty acids, and the paraffins, and to form some idea of the mode in which substances of these groups are formed in nature, there has been hitherto no direct connection established between the carbohydrates and the benzene family, much less with the terpenes and resins which are so abundant

in the vegetable kingdom. Now, however, it is shown that the heptine, C_7H_{12}, obtained by reducing perseïtol with boiling hydriodic acid, and therefore a product of direct synthesis, is not only identical with the heptine extracted by Renard from resin oil, but has the characteristic properties of the terpenes, and may, in fact, be regarded as a lower member of that, or perhaps of the menthene, family.

Heptine is very oxidisable, resinifies in air, forms a crystalline hydrate with water, $C_7H_{14}O_2$, homologous with terpene hydrate, $C_{10}H_{20}O_2$, unites directly with bromine and hydrogen chloride and iodide to form compounds, $C_7H_{12}Br_2$, $C_7H_{13}Cl$, $C_7H_{13}I$, and forms a nitrosochloride, $C_7H_{12}NOCl$. Hence there is little doubt as to its nature. Further confirmation is given by the fact that the differences between the observed and calculated molecular refractions for wave lengths $H\alpha$ and ∞ are 2·15 and 1·97, numbers which agree closely with 1·78 and 1·60, those found by Brühl and Landolt to hold for single ethylene linkings. Hence heptine is built on a cycloïd nucleus, probably intermediate between benzene and hexamethylene. It is especially interesting as the first example of a complete synthesis effected in the terpene group, other than by polymerisation of a simpler hydrocarbon, and seeing that the synthesis has been effected directly from a natural carbohydrate, it opens up a suggestive field of speculation around the processes occurring in nature.

Heptine nitrosochloride, $C_7H_{12}NOCl$, is formed by adding solid sodium nitrite gradually to a cooled mixture of heptine and hydrochloric acid. The supernatant layer turns green, crystallises, is removed, cautiously drained and washed at the pump, and finally dried in a vacuum. The nitrosochloride thus prepared consists of a mass of pale-blue, microscopic needles, and has a strong odour of camphor; it melts about 92° with partial volatilisation and decomposition. It is very unstable, and can be kept only for a few hours; even in a vacuum it soon resinifies. Jn. W.

Terpin Hydrate from Eucalyptus Oil. By E. Merck (*Arch. Pharm.*, **230**, 169—173).—The terpin hydrate, produced by mixing turpentine oil with nitric acid and alcohol and setting it aside for some time (Wallach, Abstr., 1886, 70), is also produced when eucalyptus oil is similarly treated. The author has not yet succeeded in discovering which constituent of the oil yields the terpin hydrate; both *Ol. eucalypt. globuli* and *Ol. eucalypt. Australe* give the reaction, but there is little or no evidence that any sample of eucalyptus oil, as supplied by the trade, is from only one source. A. G. B.

Oil of Lavender and of Bergamot. By J. Bertram and H. Walbaum (*J. pr. Chem.* [2] **45**, 590—603).—French lavender oil consists for the most part of an alcohol, $C_{10}H_{18}O$, and ethereal salts, chiefly the acetate, derived therefrom. In its reactions and physical properties this alcohol is identical with linalol obtained by Semmler from linaloes (Abstr., 1891, 540); it absorbs 4 atoms of bromine, yields the chloride, $C_{10}H_{18}Cl_2$, with hydrogen chloride, and is oxidised to citral (geranaldehyde, *loc. cit.*) by chromic acid mixture. De-

hydrating agents eliminate from the alcohol, hydrocarbons of the formula $C_{10}H_{16}$, among which terpinene and dipentene are to be recognised.

Bergamot oil also contains the acetate derived from linalol, and owes its odour to this. A. G. B.

Essential Oil of Licari Kanali. By P. Barbier (*Compt. rend.*, **114**, 674—675).—The essential oil of *Licari kanali* was found by Morin to contain a substance, $C_{10}H_{18}O$, which the present author terms *licareol*. It is a colourless, somewhat oily liquid, which boils at 199—200°, and has a sp. gr. of 0·8819 at 0°, and 0·8662 at 15·4°. Its rotatory power at 15·4° is $[\alpha]_D = -18° 21'$, and its refractive indices at the same temperature are 1·4635 for the red, and 1·4775 for the blue rays. It reacts with dry hydrogen chloride to form a liquid *dichloro-derivative*, $C_{10}H_{18}Cl_2$, which boils at 155—157° under a pressure of 39 mm., and has a sp. gr. of 1·0447 at 0°, and 1·0246 at 19·5°, and refractive indices 1·4789 for the red, and 1·4926 for the blue rays at 17·2°. When the dichloro-compound is boiled with a solution of potassium acetate in glacial acetic acid, it loses its chlorine, and is converted into an *acetate*, $C_{10}H_{17}OAc$, which is also formed when licareol is heated with acetic anhydride in a sealed tube for eight hours at 140°, and is a colourless liquid of agreeable odour, boiling at 241—242°, and having a density of 0·9298 at 0°. It is not the acetate of licareol, since the difference between its boiling point and that of the parent substance is much greater than the normal, and when, moreover, it is hydrolysed, it yields an isomeric alcohol boiling at 226—227°.

Along with the acetate there are also formed an ether, $(C_{10}H_{17})_2O$, which is a viscous, colourless liquid, boiling with partial decomposition at 320°, and a liquid hydrocarbon, $C_{10}H_{16}$, which boils at 176—178°.

The methyl and ethyl derivatives of licareol, *methyl licaryl ether*, $C_{10}H_{17}\cdot OMe$, and *ethyl licaryl ether*, are liquids boiling at 189—192°, and at about 210°.

Licareol is energetically attacked by chromic acid mixture, and among the products of oxidation a ketone, *licareone*, $C_{10}H_{16}O$, occurs as a liquid of penetrating odour, boiling at 188—190°, and having a density of 0·8913 at 0°. It does not combine with sodium bisulphite, but it reduces alcoholic ammoniacal silver nitrate, and combines with hydroxylamine to form a liquid oxime. It therefore contains two secondary alcohol groups and an ethylene bond. Jn. W.

Studies in the Camphor and Fenchone Series. By O. Wallach (*Annalen*, **269**, 326—347; compare Abstr., 1891, 218 and 1086).—The compound (fenchonitrile) of the composition $C_{10}H_{15}N$, obtained by treating the oxime of fenchone (fenchole) with dilute sulphuric acid, behaves just like an unsaturated compound, and combines directly with the halogen acids to form rather unstable, crystalline, additive products. The *bromo*-compound, $C_9H_{16}Br\cdot CN$, melts at 60°; the *iodo*-compound, $C_9H_{16}I\cdot CN$, at 54—55°; and the *chloro*-compound, $C_9H_{16}Cl\cdot CN$, at 57—58°; the last-named compound is, in the

dry state, the most stable of the three, but is readily decomposed when boiled with alcohol or water.

Camphonitrile, $C_{10}H_{15}N$, boils at 226—227°, and has a sp. gr. of 0·910 at 20°. Its refractive power is $n_{(D)} = 1·46648$ at 20°, from which M = 45·39; this number agrees with the value calculated on the assumption that the nitrile contains a single double-linking. Camphonitrile behaves chemically like an unsaturated compound, and combines directly with halogen acids, but the products do not crystallise.

β-Isofenchonoxime, $C_{10}H_{17}NO$, is obtained when the α-isofenchonoxime (m. p. 113—114°) previously described (*loc. cit.*) is boiled for a few hours with dilute sulphuric acid, and the cold solution then neutralised with an alkali. It crystallises well from alcohol and hot water, melts at 137°, distils unchanged, and is much more readily soluble in hot water than the α-oxime; it has a pronounced basic character, forms with hydrogen chloride in ethereal solution a colourless, unstable hydrochloride, and, like the α-oxime, is only very slowly acted on by boiling alcoholic potash. When warmed with phosphorus pentoxide, it seems to be converted into fenchonitrile, and on oxidation with potassium permanganate, it yields, like fenchone, dimethylmalonic acid.

Fencholenic acid, $C_{10}H_{16}O_2$ (*loc. cit.*), boils at 260—261°, and has a sp. gr. of 1·0045 at 16°; its refractive power is $n_{(D)} = 1·4768$, from which M = 47·24, the calculated value being M = 47·34. The *ammonium* salt, prepared by passing anhydrous ammonia into an ethereal solution of the acid, is a colourless, very hygroscopic powder. The *silver* salt, $C_{10}H_{15}O_2Ag$, is a colourless, comparatively stable powder, sparingly soluble in water and alcohol. The acid is unsaturated, and combines with concentrated hydriodic acid to form a crystalline additive compound. The corresponding *chloro*-compound, $C_{10}H_{17}ClO_2$, prepared by shaking fencholenic acid with concentrated hydrochloric acid, is more stable than the iodo-additive product, and separates from light petroleum in small crystals which melt at 97—98°; it is readily decomposed by alkalis. When fencholenic acid is distilled with soda-lime, it yields an oil, which consists of a mixture of hydrocarbons and compounds containing oxygen.

Campholenic acid boils at 258—261°, and its sp. gr. is 0·9920 at 19°; its refractive power is $n_{(D)} = 1·47125$, from which M = 57·36; its electrical conductivity is K = 0·00170, that of fencholenic acid being K = 0·00100. Campholenic acid is unsaturated, and combines with bromine in alcoholic or glacial acetic acid solution, yielding a crystalline substance, which is insoluble in alkalis.

An *acid* of the composition $C_{10}H_{18}O_4$ is formed when campholenic acid is oxidised with potassium permanganate in alkaline solution; it separates from hot water in transparent crystals, melts at 144—145°, and distils without appreciable decomposition; its electrical conductivity is K = 0·00250. The *silver* salt, $C_{10}H_{17}O_4Ag$, is amorphous, and moderately easily soluble in water.

A saturated *hydrocarbon*, which has probably the molecular formula C_9H_{18}, is produced when fencholenic acid is heated with concentrated hydriodic acid and amorphous phosphorus at 180—200°; it boils at

141—142°; its sp. gr. is 0·7900 at 20°, and its refractive power $n_{(D)} = 1·43146$. The same hydrocarbon appears to be obtained when fenchonitrile is reduced in like manner.

When campholenic acid is heated with concentrated hydriodic acid and amorphous phosphorus, it is converted into a saturated *hydrocarbon*, which boils at 134—136°, and seems to have the molecular formula C_9H_{18}; the sp. gr. of this hydrocarbon is 0·773 at 20°, and its refractive power $n_{(D)} = 1·42491$.

These experiments show that in both campholenic acid and fencholenic acid there is a closed carbon chain, and only one double linking; this is also true as regards camphonitrile and fenchonitrile.

F. S. K.

Comparison of Bornylamine and Fenchylamine. By O. Wallach and J. Griepenkerl (*Annalen*, **269**, 347—369).—*Bornylamine tartrate*, $C_{10}H_{17}·NH_2,C_4H_6O_6 + H_2O$, crystallises from hot alcohol in needles, and is readily soluble in water. The *picrate*, $C_{10}H_{17}·NH_2,C_6H_3N_3O_7$, crystallises in yellow needles, and is readily soluble in alcohol, but almost insoluble in ether. The hydrochloride sublimes at a high temperature without decomposition.

When bornylamine, or its formyl derivative, is heated with acetic anhydride at 200—210°, it is converted into camphene; when formylbornylamine is boiled with an aqueous solution of chromic acid, it yields bornylamine and a very volatile crystalline compound, which melts at 159°, and contains oxygen.

Dibornylthiocarbamide, $CS(NH·C_{10}H_{17})_2$, is formed when bornylamine is boiled with carbon bisulphide and alcohol; it separates from alcohol in transparent crystals, and melts at 223—224°.

Benzylbornylamine, $C_{10}H_{17}·NH·CH_2Ph$, is a thick oil, boiling at 184° under a pressure of 14 mm.; its *hydrochloride*, $C_{17}H_{25}N,HCl$, separates from water and alcohol in colourless crystals; its *platinochloride*, $(C_{17}H_{25}N)_2,H_2PtCl_6$, crystallises in transparent, red prisms, and is almost insoluble in water; its *methiodide*, $C_{17}H_{25}N,MeI$, crystallises from hot alcohol in needles.

Benzylidenebornylamine, $C_{10}H_{17}N{:}CHPh$, is a colourless oil, but its *hydrochloride*, $C_{17}H_{23}N,HCl$, crystallises in small needles.

Dibornylamine, $C_{20}H_{35}N$, a compound which was first isolated by Leuckart (Abstr., 1887, 376), from the product of the action between camphor and ammonium formate, crystallises from alcohol in lustrous plates, melts at 43—44°, and boils at 180—181° under a pressure of 12 mm.; molecular weight determinations by the boiling point method gave results agreeing with those required by a compound of the molecular formula given above. Although dibornylamine has a neutral reaction towards litmus, it combines with hydrogen chloride in ethereal solution to form the *hydrochloride*, $C_{20}H_{35}N,HCl$; this compound crystallises in needles or plates, melts at 260° with partial decomposition, and is readily soluble in hot, but only sparingly in cold, water; the *platinochloride*, $(C_{20}H_{35}N)_2,H_2PtCl_6$, crystallises from alcohol in red needles. The *nitrite*, $C_{20}H_{35}N,HNO_2$, crystallises unchanged from boiling alcohol, and is only moderately easily soluble in water. The *nitrate* is very sparingly soluble in water.

When dibornylamine is treated with bromine in light petroleum solution, a *salt* of the composition $C_{20}H_{35}Br_2N,HBr$ is precipitated; it crystallises from alcohol in golden plates, melts at 184°, and is reconverted into dibornylamine on treatment with sulphurous acid and an alkali. Dibornylamine seems not to give an acetyl or a benzoyl derivative; on prolonged heating with acetic anhydride at 100—130°, it is transformed into a crystalline substance which melts at 59°, and seems to be an isomeride.

Fenchylamine hydriodide, $C_{10}H_{17}\cdot NH_2,HI$, crystallises well, and is moderately easily soluble in water and dilute alcohol; both the hydrochloride (Abstr., 1891, 1086) and the *picrate* are readily soluble in ether. The *tartrate* is very sparingly soluble in alcohol. The *nitrite*, $C_{10}H_{17}\cdot NH_2,HNO_2$, crystallises in lustrous needles, is very readily soluble in water, and decomposes at 100—115°.

Fenchylcarbamide, $NH_2\cdot CO\cdot NH\cdot C_{10}H_{17}$, crystallises from water and dilute alcohol in small needles, and melts at 170—171°.

Fenchylphenylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{17}$, is formed when fenchylamine is treated with phenylthiocarbimide in ethereal solution; it separates from alcohol in colourless, well-defined crystals, and melts at 153—154°.

Difenchylthiocarbamide, $CS(NH\cdot C_{10}H_{17})_2$, crystallises in colourless plates, and melts at 210°.

Acetylfenchylamine, $C_{10}H_{17}\cdot NHAc$, melts at 98°, not at 92·5° as previously stated (*loc. cit.*); the benzoyl derivative, $C_{10}H_{17}\cdot NHBz$, melts at 133—135°, not at 89·5°.

Benzylfenchylamine, $C_{10}H_{17}\cdot NH\cdot CH_2Ph$, is a thick oil of sp. gr. 0·9735 at 20°, and boils at 190—191° under a pressure of 16 mm. The *hydrochloride*, $C_{17}H_{25}N,HCl$, separates from water in well-defined crystals. The *platinochloride*, $(C_{17}H_{25}N)_2,H_2PtCl_6$, separates from alcoholic hydrochloric acid in ruby-red crystals. The nitroso-derivative, $C_{10}H_{17}N(NO)\cdot CH_2Ph$, crystallises from alcohol and ether in prisms, and melts at 93°.

Benzylidenefenchylamine, $C_{10}H_{17}N{:}CHPh$, crystallises from methyl alcohol in needles, and melts at 42°. The *hydrochloride*, $C_{17}H_{23}N,HCl$, is very hygroscopic and unstable. The *platinochloride*,

$$(C_{17}H_{23}N)_2,H_2PtCl_6,$$

crystallises in yellowish-red needles, and is very unstable.

Hydroxybenzylidenefenchylamine, $C_{10}H_{17}N{:}CH\cdot C_6H_4\cdot OH$, prepared by heating fenchylamine with salicylaldehyde, crystallises in yellow needles, melts at 95°, and is readily decomposed by acids and alkalis.

When fenchylamine is treated with chloral, it is converted into formylfenchylamine (*loc. cit.*); with ethyl acetoacetate, it gives a condensation product which has the composition $C_{16}H_{27}NO_2$.

Difenchyloxamide, $C_{22}H_{36}N_2O_2$, crystallises from alcohol in long prisms or quadratic plates melting at 188°.

Fenchylamine fenchylcarbamate, $C_{10}H_{17}\cdot NH_2,C_{10}H_{17}\cdot NH\cdot COOH$, is formed when carbonic anhydride is passed into an alcoholic solution of fenchylamine; it separates from alcohol in crystals, and is almost insoluble in water.

Methylfenchylamine, $C_{10}H_{17}\cdot NHMe$, is an oil of sp. gr. 0·8950 at

20·5° ; it boils at 201—202°, has a refractive power $n_{(D)} = 1·46988$ at 20·5°, and is only sparingly soluble in water. The *hydriodide*, $C_{11}H_{21}N,HI$, is only very sparingly soluble in water. The *hydrochloride*, $C_{11}H_{21}N,HCl$, forms prismatic crystals, and is insoluble in ether. The *platinochloride*, $(C_{11}H_{21}N)_2,H_2PtCl_6$, is crystalline. The *nitroso*-derivative, $C_{10}H_{17}·NMe·NO$, is a crystalline compound melting at 52—53°. F. S. K.

Fencholenamine. By O. Wallach and L. Jenckel (*Annalen*, **269**, 369—376; compare Abstr., 1891, 1086).—*Fencholenamine*, $C_{10}H_{17}·NH_2$, is obtained, together with compounds of higher boiling point, when fenchonitrile is reduced with sodium and alcohol; it is a mobile oil, and boils at 205°. The *nitrate*, $C_{10}H_{17}·NH_2,HNO_3$, separates from water in crystals. The *sulphate*, $(C_{10}H_{17}·NH_2)_2,H_2SO_4$, crystallises in colourless plates, and is sparingly soluble in water. A compound of the composition $C_{10}H_{21}Cl_2N$ is precipitated in crystals when hydrogen chloride is passed into a methyl-alcoholic solution of fencholenamine; when treated with alkalis, it loses nearly the whole of its chlorine. The *benzoyl* derivative, $C_{10}H_{17}·NHBz$, separates from alcohol in crystals, and melts at 88—89°. The *acetyl* derivative, $C_{10}H_{17}·NHAc$, is an oil, and boils at 180° under a pressure of 21 mm. When fencholenamine is treated with sodium nitrite and dilute sulphuric acid, it yields, as principal product, an oil of the composition $C_{10}H_{18}O$, which is probably fencholen alcohol; this compound boils at 96° under a pressure of 17 mm., has a sp. gr. of 0·8980 at 20°, and a refractive power $n_{(D)} = 1·4739$ at the same temperature; it has a strong odour of terpineol, and seems to be only slowly oxidised by chromic acid. F. S. K.

Camphene and Camphoric Acid. By J. W. Brühl (*Ber.*, **25**, 2087—2095).—This paper is of a purely controversial nature, being an answer to Wallach (this vol., p. 868). The author maintains the accuracy of the value observed by him for the melting point of borneocamphene (this vol., p. 624) against that given by Wallach, and he is of opinion that the difference in the value is due to the greater purity of his own preparation. Wallach (*loc. cit.*) has reassured himself as to the efficiency of his method of preparing the camphene by heating bornyl chloride with aniline; the author complains, however, that information as to the yield obtained is wanting. It is shown by the aid of formulæ that Wallach's objection to the tetramethylene formula for camphoric acid, on the ground that it is difficult to explain the formation of hydrogenised metaxylenes from the latter, is unfounded. A. R. L.

Absinthin from Artemisia absinthum. By O. Senger (*Arch. Pharm.*, **230**, 94—108).—Pure absinthin is best prepared by shaking the ethereal extract of the plant with water, and treating the aqueous solution with freshly-precipitated aluminium hydroxide; the solution may then be directly evaporated in a vacuum or shaken with ether, and the ethereal solution subsequently distilled. Absinthin, $C_{15}H_{20}O_4$, is pale yellow and amorphous; it has an intensely bitter

taste, melts at 65°, and dissolves in water, alcohol, and ether. It is a glucoside, being decomposed by hydrolysis into dextrose, a liquid substance, and a resinous compound, $C_{21}H_{26}O_6$, which belongs to the aromatic series, and behaves like a hydroxy-acid. Phloroglucinol is one of the products of the decomposition of absinthin by alkalis, and formic, acetic, and propionic acids occur among the products of its oxidation by potassium dichromate and sulphuric acid. With concentrated nitric acid, it yields oxalic and picric acids. A. G. B.

Anemonin. By H. Beckurts (*Arch. Pharm.*, **230**, 182—206).—Several species of *Anemone* and *Ranunculus* owe their acrid taste to the presence of anemone-camphor (Abstr., 1886, 365); this readily decomposes, even during the drying of the plant, into anemonin and isoanemonic acid. There are also obtained from the plant anemonic acid and anemoninic acid.

Anemonin, $C_{10}H_8O_4$, melts at 152°; its new formula (compare *loc. cit.*) was determined by the cryoscopic method. It would appear to be the anhydride of anemonic acid, into the lead salt of which it is easily converted by treatment with lead oxide. By dilute acids and by alkalis, it is converted into anemoninic acid and its salts. It would appear to contain both an aldehyde and a ketone group, for it yields the characteristic reactions with phenylhydrazine, hydroxylamine, sodium hydrogen sulphite, and sodium nitroprusside; a hydroxyl or oxalyl group could not be recognised. The *amide*, $C_{10}H_{15}N_3O_3$, a yellow, microcrystalline powder, which melts at 68—69°, and is soluble in alcohol and water, is formed when anemonin is heated with alcoholic ammonia. When anemonin is heated with acetic anhydride, it becomes *isoanemonin*, a yellowish-white powder insoluble in the usual solvents. When acted on by bromine in chloroform, anemonin yields the tetrabromide, $C_{10}H_8Br_4O_4$; this is a white, crystalline powder which begins to melt at 180°, and melts with decomposition at 205°.

Anemonic acid, $C_{10}H_{10}O_5$, crystallises in hard, white needles, and melts at 210°; it has an acid reaction, is bibasic, and forms colourless salts, of which the *lead salt* was prepared. It contains an aldehyde or ketone group. *Isoanemonic acid* is produced during the isolation of anemonic acid; it is tasteless, inodorous, amorphous, and insoluble in water, alcohol, and ether.

Anemoninic acid, $C_{10}H_{12}O_6$, is a brownish-white powder, easily soluble in water, and acid to test paper. It is bibasic, its constitution being probably $C_7H_8(COOH)_2{\cdot}C(OH)_2$; its *sodium*, *potassium*, *barium*, and *lead* salts were prepared, and found to be amorphous. It reduces Fehling's solution and silver solution, and forms an amorphous *phenylhydrazide*. A. G. B.

Digitalonic Acid. By H. Kiliani (*Ber.*, **25**, 2116—2118).—The author has recently shown (*Arch. Pharm.*, **230**, 250) that when the sugars which are obtained from pure digitalin are oxidised by means of bromine, *d*-gluconic acid and digitalonic acid, $C_7H_{14}O_6$, are formed; if, however, the hydrolysis of digitalin be accomplished in two stages, the sugar yielding digitalonic acid is formed in the second stage.

It is more convenient to separate the digitalonic and *d*-gluconic acids by the following method than by that previously given (*loc. cit.*). The solution containing the two acids is evaporated to a thin syrup, mixed with one-third its weight of 93 per cent. alcohol, and shaken four times with ether, when the digitalonic lactone is extracted, and may be purified by recrystallisation from water. It forms short, rhombic crystals, $a : b : c = 0{\cdot}9243 : 1 : 0{\cdot}3662$, does not reduce alkaline copper solution, and has a specific rotatory power $[\alpha]_{D28^\circ} = -79{\cdot}4$. When the lactone is heated with excess of silver oxide at 50° for 14 hours, hydrochloric acid continuously added, and the filtrate distilled, acetic acid passes over; the presence of a methyl group in digitalonic acid is therefore probable. The research is proceeding.

A. R. L.

Origin of the Colouring Matters of the Vine: Ampelochroïc Acids. By A. Gautier (*Compt. rend.*, **114**, 623—629).—The rapidity with which grapes ripen in Mid Europe led the author to suppose that the skin pigment to which the colour is due is formed by the oxidation of aldehydic or catecholic substances, originating in the leaves and travelling thence to the fruit. This view was borne out by the effects following the removal of the leaves from grapes about to ripen, or by the partial or complete stoppage of the circulation between the leaves and stem, the grapes in the first case remaining in a state of arrested development, whilst in the second the leaves changed in colour to red or brown, and not the grapes.

The colouring matter of leaves thus reddened (from plants of the Carignan stock) was extracted with tepid water and purified by fractional precipitation with lead acetate, with which it finally formed an olive-green precipitate; this, on decomposition with hydrogen sulphide and purification, yielded a mixture of two coloured crystalline acids, α- and β-ampelochroïc acids. These were separated by means of cold water, in which the latter alone is soluble.

α-Ampelochroïc acid, $C_{19}H_{16}O_{10}$, is bibasic and forms a cochineal-coloured powder consisting of ruby-red plates or spindles, soluble in boiling water or cold alcohol, but insoluble in ether. Its solutions are feebly acid to litmus. The *zinc* salt is olive-green, and turns indigo-blue on heating; the *acid zinc* salt is rose-coloured and soluble; the *lead* salt is dark green, and blackens at 50°; the *acid lead* salt is wine red. Solutions of α-ampelochroïc acid are turned greenish-brown by alkalis, and oxidise on exposure to the air; they are precipitated by bromine-water; they give a greenish-black precipitate with ferric salts, a dark-brown precipitate with mercuric nitrate, a yellowish-grey precipitate with silver nitrate, especially in presence of ammonia, a rose-coloured precipitate with gelatin solution, and a chestnut-brown precipitate with cinchonine acetate. The acid therefore belongs to the classes of tannins and polyphenolic substances.

β-Ampelochroïc acid, which is stated to have the composition $C_{26}H_{24}O_{15}$, bears a general resemblance to the α-acid. It forms cochineal-coloured crystals, and its aqueous solution is feebly acid to litmus and feebly astringent to the taste. It is precipitated by gelatin and by cinchonine acetate; it gives a violet precipitate with tartar emetic, a dark green precipitate with zinc acetate, a dirty, rose-

coloured precipitate with mercuric nitrate, a yellowish-brown precipitate with copper acetate, and a chestnut-brown precipitate with hot silver nitrate. Potash turns the colour of its solution to yellowish-green, and ferric chloride gives a dark violet coloration, changing to a brown precipitate.

A third acid of the same general character as the others was obtained from the first fraction or blue precipitate formed in their preparation. The precipitate was suspended in water, decomposed with hydrogen sulphide, partially saturated with baryta-water, and the whole evaporated to dryness in a vacuum. The residue was extracted with ether to remove impurities, and the new acid was dissolved out with alcohol.

γ-Ampelochroïc acid, $C_{17}H_{18}O_{10}$, crystallises in reddish-brown octahedra and dissolves readily in water to a red solution, astringent to the taste. With gelatin and tartar emetic, it forms rose-coloured precipitates which dissolve on heating; with mercuric nitrate, it gives a pale, greenish-blue precipitate, a green precipitate with calcium acetate, an olive-green precipitate with basic lead acetate, a dark violet to brown precipitate with ferric salts, and an orange to yellow precipitate with bromine-water. Potash changes the colour of its solutions to olive-green. Jn. W.

Synthesis of Tetrahydropyridine Derivatives and Conversion of the same into Piperidine Derivatives. By A. Lipp (*Ber.*, **25**, 2190—2197).—Δ^2-*Tetrahydropicoline* (Δ^2-*Tetrahydro*-2-*methylpyridine*), C_6NH_8Me, is obtained by the action of aqueous or alcoholic ammonia on bromobutyl methyl ketone. It is a colourless liquid, boils at 131—132° at 716 mm., has an odour resembling that of piperidine, dissolves easily in water, and turns brown on exposure to the air. The *platinochloride*, $(C_6H_{11}N)_2,H_2PtCl_6$, crystallises in small prisms or rhombic tablets, melts and decomposes at 193—194°, and is somewhat easily soluble in water, very sparingly so in alcohol. The *aurochloride* forms small, fern-like crystals, melts at 144—145°, and is sparingly soluble in water. The *picrate* crystallises in yellow needles or short prisms, and melts at 119—120°. The base also yields a nitroso-compound and a well crystallised thiocarbamate. The base is probably identical with Ladenburg's α-pipecoleïn (*Ber.*, **20**, 1645). When reduced with tin and hydrochloric acid, it yields α-methylpiperidine. The latter agrees in properties with α-methylpiperidine prepared from picoline.

1-*Methyl*-Δ^2-*tetrahydropicoline* or 1 : 2-*dimethyl*-Δ^2-*tetrahydropyridine*, $C_5NH_7Me_2$, is obtained by the action of methylamine on the bromide of acetobutyl alcohol. It is a colourless, strongly refractive liquid, has an odour resembling that of piperidine, boils at 145° under 720 mm. pressure, turns brown when kept, and slowly dissolves in water. The *platinochloride* forms short prismatic crystals, melts at 200—205° with decomposition, and is somewhat easily soluble in water and insoluble in strong alcohol. The *aurochloride* crystallises in aggregates resembling ammonium chloride, melts at 180—182°, and is easily soluble in hot water, sparingly so in cold. The *picrate* crystallises in yellow, lustrous prisms, and is somewhat easily soluble in cold water. The

base combines with methyl iodide to yield the hydriodide of an ammonium base. When reduced with tin and hydrochloric acid, it yields *n*-*α*-dimethylpiperidine. The latter was also prepared from *α*-methylpiperidine. Both preparations had the same properties.

1-*Phenyl*-Δ^2-*tetrahydropicoline* or 1-*phenyl*-Δ^2-*tetrahydro*-2-*methylpyridine*, $C_5NH_7MePh + H_2O$, is obtained by the action of aniline on bromobutyl methyl ketone. It crystallises in colourless prisms or tablets, melts at 54—55°, decomposes when heated at its boiling point, and is odourless at the ordinary temperature, but at higher temperatures has a peculiarly characteristic odour. It is insoluble in cold water, sparingly soluble in hot water and cold light petroleum, easily so in alcohol, ether, and hot light petroleum. The *hydrochloride* is hygroscopic. With platinic chloride and picric acid, it yields well crystallised compounds, and combines with methyl iodide with evolution of heat.

Dimethylacetobutylamine, $COMe\cdot[CH_2]_4\cdot NMe_2$, is obtained by the action of dimethylamine on bromobutyl methyl ketone. It is a colourless liquid, having a faint ammoniacal odour, boils at 195° under 720 mm. pressure, and is easily soluble in water, ether, and alcohol. The *hydrochloride* is very hygroscopic. The *aurochloride* and the *platinochloride* were not obtained crystalline. The *picrate* crystallises in yellow leaflets, and is sparingly soluble in cold water. The base combines with hydroxylamine hydrochloride and with phenylhydrazine with development of heat. E. C. R.

1-Methyl-Δ^2-tetrahydro-2-hydroxyethylpyridine. By A. Lipp (*Ber.*, **25**, 2197—2200).—1-*Methyl*-Δ^2-*tetrahydro*-2-*hydroxyethylpyridine*, $CH_2<\begin{matrix}CH_2—CH\\CH_2\cdot NMe\end{matrix}>C\cdot CH_2\cdot CH_2\cdot OH$, is formed on gradually adding formaldehyde to 1-methyltetrahydropicoline dissolved in twice its weight of water and allowing the mixture to remain; it is then distilled in a current of steam, the distillate acidified with hydrochloric acid, evaporated, and the hydrochloride of the base decomposed with potassium hydroxide. It is a colourless, limpid liquid, turns brown on exposure to the air, has a faint ammoniacal odour, boils at 198—199° under 710 mm. pressure, dissolves in water in all proportions, and is not solid at −20°. The *hydrochloride* is very easily soluble in water, and melts at 155—157°. The *aurochloride* crystallises in leaflets, melts at 119—121°, and is easily soluble in hot, sparingly so in cold water. The *platinochloride* crystallises in needles, melts at 200—205° with decomposition, and is sparingly soluble in water, insoluble in alcohol. The *picrate* crystallises from water in small prisms, and from alcohol in long, lustrous needles, and melts at 126—127°. The *mercurochloride*, $C_8H_{15}ON,HCl + 6HgCl_2$, forms small, lustrous crystals, melts at 161—162° with decomposition, and is sparingly soluble in water.

The above methyltetrahydrohydroxyethylpyridine should have similar properties to tropine if the latter has the constitution assigned to it by Ladenburg. This is not the case, however, and the author considers that Merling's formula for tropine is the correct one.

The above base is easily reduced with sodium and alcohol, and the

reduction product should be identical with Ladenburg's 1-methylpipecolylalkine (*Ber.*, **24**, 1622), which, however, is not the case.

1-*Methylpipecolylalkine*, prepared from the above base, is a syrupy liquid having a faint ammoniacal odour, boils at 215—216° under 720 mm., is strongly alkaline, and is very soluble in water and alcohol, more sparingly so in ether. The *hydrochloride* crystallises in colourless needles and prisms, and is very hygroscopic. The *platinochloride* was not obtained crystalline. The *aurochloride*,

$$C_7H_{14}MeON,HAuCl_4,$$

crystallises in small leaflets, begins to coagulate at 120°, melts at 127—128°, and is somewhat easily soluble in warm water. The *double salt* with *mercuric chloride*, $C_8H_{17}NO,HCl,6HgCl_2$, forms small, lustrous crystals, and melts partially at 165—166° with decomposition. E. C. R.

Synthesis of Quinaldine. By W. v. Miller (*Ber.*, **25**, 2072—2074; see also Abstr., 1891, 1101).—Under the conditions of the quinaldine synthesis, it is probable that ethylidene- and propylideneaniline occur as bimolecular secondary bases. When ethylideneaniline and propylideneaniline are heated with hydrochloric acid, they are converted into quinaldine and α-ethyl-β-methylquinoline respectively, the reaction taking place in the four stages—

$$NPh{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}NHPh, \qquad NHPh{\cdot}CH\!<\!\begin{matrix}CH_2\cdot CHMe\\ |\\ C_6H_4\cdot NH\end{matrix},$$

$$NH_2Ph + CH\!<\!\begin{matrix}CH-CHMe\\ |\\ C_6H_4\cdot NH\end{matrix}, \text{ and } CH\!<\!\begin{matrix}CH-CMe\\ ||\\ C_6H_4\cdot N\end{matrix} + 2H.$$

Only 22 per cent. of the theoretical yield is, however, obtained. E. C. R.

Methylphenylpyrazolone and its Derivatives. By C. Möllenhoff (*Ber.*, **25**, 1941—1951).—Methylphenylpyrazolonesulphonic acid, $SO_3H{\cdot}C_6H_4{\cdot}N\!<\!\begin{matrix}N=CMe\\ |\\ CO\cdot CH_2\end{matrix}$, is best prepared by heating methylphenylpyrazolone with 30 per cent. anhydrosulphuric acid (4 parts) on the water-bath; the product is added to water, when the acid separates in the crystalline state. It crystallises from water in small needles, containing 1 mol. H_2O, darkens at 290°, and decomposes at 320°; it is sparingly soluble in alcohol and glacial acetic acid, more readily in water, but is insoluble in ether. It reduces Fehling's solution on warming, does not give pyrazole blue (Knorr, Abstr., 1887, 602) on heating with ferric chloride, but a red coloration, which is destroyed by boiling or on the addition of hydrochloric acid. The *calcium* and *barium* salts were prepared, but on attempting to prepare the silver salt by means of silver carbonate, metallic silver was produced. The same sulphonic acid is obtained when paraphenylhydrazinesulphonic acid is heated with an excess of ethyl

acetoacetate at 150—160°. When a solution of the acid is boiled with bromine (3 mols.), *methylbromophenyldibromopyrazolone*,

$$C_6H_4Br\cdot N<\begin{matrix}N{=}CMe\\ |\\ CO\cdot CBr_2\end{matrix}>,$$

melting at 83·5°, is formed; the same compound is furnished when the methylphenylpyrazolone, dissolved in glacial acetic acid, is brominated. The corresponding trichloro-derivative is obtained on passing chlorine through a solution of the sulphonic acid. When the methylphenylpyrazolone is heated at 120° with a large excess of bromine, a tetrabromo-derivative melting at 134—135° is produced.

The *compound* $SO_3H\cdot C_6H_4\cdot N<\begin{matrix}N{=}CMe\\ |\\ CO\cdot C{:}N_2HPh\end{matrix}$ separates as an oil, which subsequently solidifies when the calculated quantity of diazobenzene chloride solution is added to a strongly alkaline solution of the above mentioned sulphonic acid, with cooling; it crystallises from acetic acid in small, brownish-yellow crystals, melts at 262° with decomposition, dyes wool yellow, and is readily soluble in water and alcohol.

Dichloromethylphenylpyrazolonesulphonic chloride,

$$SO_2Cl\cdot C_6H_4\cdot N<\begin{matrix}N{=}CMe\\ |\\ CO\cdot CCl_2\end{matrix}>,$$

is prepared by heating the sulphonic acid (1 mol.) with phosphorus pentachloride (3 mols.) on the water-bath, distilling off phosphorus compounds under diminished pressure, and crystallising the residue from benzene. The pure compound is sparingly soluble in ether and light petroleum, and melts at 103·5°; when heated at 50° with sodium ethoxide, it yields the compound $SO_2Cl\cdot C_6H_4\cdot N<\begin{matrix}N{=}CMe\\ |\\ CO\cdot C(OEt)_2\end{matrix}>,$ which crystallises from alcohol in small, reddish needles, melts at 68°, and gives the corresponding sulphonic acid on boiling with water.

When methylphenylpyrazolonesulphonic acid is fused with potash, phenol is formed. The blue *colouring matter*,

$$SO_3H\cdot C_6H_4\cdot N<\begin{matrix}N{=}CMe & CMe{:}N\\ |\\ CO\cdot C{=}{=}C{-}CO\end{matrix}>N\cdot C_6H_4\cdot SO_3H,$$

is prepared by passing bromine vapour (avoiding excess) into an aqueous solution of bismethylphenylpyrazolonedisulphonic acid (Knorr, *Annalen*, **238**, 170), and precipitating with a saturated solution of common salt; its aqueous solution is fairly stable in the cold, but decomposes on heating.

Dimethylphenylpyrazolone (antipyrine) and the corresponding bisdimethylphenylpyrazolone give sulphonic acids when heated with 30 per cent. anhydrosulphuric acid. A. R. L.

Azonium Bases. By O. N. Witt and C. Schmidt (*Ber.*, **25**, 2003—2008).—In a former paper (*Ber.*, **25**, 1014), the authors stated that certain observations of Meldola and his pupils were not

quite in agreement with their own; they, however, now acknowledge having erroneously compared their own work on the reduction of anilineazo-α-naphthol derivatives with that of Meldola and his pupils on the corresponding β-naphthol derivatives.

When ethoxyphenylnaphthostilbazonium chloride (this vol., p. 863) is heated with an excess of alcoholic ammonia in a sealed tube at 120°, and the melt dissolved in boiling dilute acetic acid, hydrochloric acid precipitates a substance which is the hydrochloride of a saffranine base, and, after purification, forms small, scarlet needles having a green reflex; it dyes silk, wool, and cotton a rose colour, dissolves in water and alcohol forming a scarlet solution with a greenish-red fluorescence, and in concentrated sulphuric acid forming a reddish-violet solution, which, on the addition of water, changes successively to green, red, and orange, and has the constitution $NH_2\cdot C_{10}H_5<\begin{matrix}NPhCl\cdot CPh\\ |\quad\quad\quad ||\\ N\text{——}CPh\end{matrix}$.

The corresponding *paratoluidine* derivative,

$$C_6H_4Me\cdot NH\cdot C_{10}H_5<\begin{matrix}N\cdot PhCl\cdot CPh\\ |\quad\quad\quad ||\\ N\text{——}CPh\end{matrix}',$$

is obtained by heating the ethoxy-compound in a sealed tube at 110—120° for 8—10 hours; it dyes cotton a beautiful reddish-violet, is sparingly soluble in water, and dissolves in concentrated sulphuric acid forming a slate-blue solution, which, on dilution, passes from pure blue to violet.

When ethoxyphenylnaphthostilbazonium chloride is heated to fusion, ethyl chloride distils over, and at a higher temperature *phenylnaphthostilborosindone*, $C_{10}H_5{:}O<\begin{matrix}N\cdot PhCPh\\ |\quad\quad ||\\ N\text{——}CPh\end{matrix}'$, sublimes; the latter is also formed when a solution of the stilbazonium chloride in aniline, paratoluidine, phenol, &c., is heated quickly to boiling. The rosindone is most conveniently prepared by heating the stilbazonium chloride with dimethylaniline (6 parts) when it dissolves with a carmine colour, and the new compound separates from the filtrate on cooling. It is a feeble base, its hydrochloride being decomposed by water and when heated alone at 100°. Silk is dyed red when immersed into an aqueous alcoholic solution of one of its salts. Fuming sulphuric acid converts it into a sulphonic acid which dyes silk a red colour in an acid bath. A. R. L.

Action of Ethylenediamine on Thiamides. By G. Forssel (*Ber.*, **25**, 2132—2142; compare Abstr., 1891, 1003).—The base $\begin{matrix}CH_2\text{—}N\\ |\quad\quad\\ CH_2\cdot NH\end{matrix}>C\cdot C<\begin{matrix}N\text{—}CH_2\\ |\quad\quad\\ NH\cdot CH_2\end{matrix}$ is prepared by heating dithiooxamide with ethylenediamine hydrate (2 parts) on the water-bath until the evolution of gas ceases. It crystallises from alcohol in almost colourless needles which are strongly electrical when rubbed, commence to soften at 240°, and melt between 290° and 300°; it is insoluble in benzene and ether, and sparingly soluble in cold alcohol and water.

The *hydrochloride*, $C_6H_{10}N_4,2HCl$, forms needles, insoluble in alcohol; the *platinochloride* and the *picrate* are also described; the *dinitroso-derivative*, $C_6H_8N_4(NO)_2$, obtained on adding potassium nitrite to a concentrated solution of the base in glacial acetic acid, crystallises from alcohol in greenish-white needles melting at 173° with decomposition; whilst the *diacetyl derivative* melts at 250°, and dissolves in water with decomposition.

Ethylenebenzenyldiamine, described by v. Hofmann (Abstr., 1888, 1050), is obtained by heating thiobenzamide with somewhat more than the calculated quantity of ethylenediamine hydrate. The *platinochloride* melts at 200°, the *mercurochloride* at 192—195°, and the *picrate* at 233°. The *nitroso-derivative*, melting at 66—67°, and the *benzoyl derivative* were also prepared.

β-Naphthoethylenediamine, $C_{10}H_7\cdot C\overset{NH\cdot CH_2}{\underset{N---CH_2}{|\!|}}$, is formed when β-naphthothiamide (10 parts) is heated on the water-bath with ethylenediamine hydrate (7 parts); it crystallises in short, white, opaque needles, melts at 116°, and is sparingly soluble in water, ether, and light petroleum, readily so in alcohol and benzene. The *platinochloride*. $(C_{13}H_{12}N_2)_2,H_2PtCl_6$, melts at 219—221°; the *mercurochloride*, $C_{13}H_{12}N_2,HHgCl_3$, melts at 180—186°; whilst an *additive* compound, $C_{13}H_{12}N_2,2HgCl_2$, obtained by mixing alcoholic solutions of the base and mercuric chloride, melts between 230° and 250°. The *picrate* melts at 196°, and the *nitrate* at 166—167°, whilst the *nitroso*-derivative melts at 101°, and the *acetyl* derivative at 160—166°. When the base is treated on the water-bath with acetic anhydride, a *compound*, $C_{17}H_{18}N_2O_3$, is produced, which is, perhaps, an open chain derivative.

A *base*, $C_{13}H_{12}N_2$, isomeric with that just described, is obtained by a similar process from α-naphthothiamide and ethylenediamine; it forms small, yellowish-white needles, and melts at 131°. The *platinochloride* melts at 214°, the *mercurochloride* melts at 185—190°, whilst a mercuric chloride *additive* product, corresponding with that described above, melts between 250° and 260°. The *picrate* melts at 237°, and the nitroso-derivative at 155—156°. When the base is treated with benzoic chloride by the Baumann-Schotten method, it gives a compound melting at 161°, having, probably, the constitution $C_{10}H_7\cdot CO\cdot NBz\cdot C_2H_4\cdot NHBz$ (compare Bamberger and Berlé, this vol., p. 632). A. R. L.

Phthalamidones. By A. Bistrzycki and G. Cybulski (*Ber.*, **25**, 1984—1990).—An extension of the method of preparing phthalamidones (Abstr., 1891, 746). The phthalamidones to be described crystallise from alcohol in yellow needles, and are all more or less soluble in hot alcohol, glacial acetic acid, and benzene, but insoluble, or only very slightly soluble, in water, ether, and light petroleum. They dissolve, moreover, in concentrated sulphuric acid with a yellowish-red colour, which disappears on the addition of water.

Toluylenephthalamidone, $\overset{C_6H_3Me\cdot N\cdot CO}{\underset{N=\!=\!=C\cdot C_6H_4}{|\!|}}$, is prepared from toluyl-

eneamidinebenzenylorthocarboxylic acid, and melts at 188°; *bromotoluylenephthalamidone*, $\begin{matrix} C_6H_2MeBr\cdot N\cdot CO \\ | \quad\quad\quad | \quad | \\ N\text{———}C\cdot C_6H_4 \end{matrix}$, formed from the bromo-acid, melts at 212—213°.

αβ-Naphthylenedimethoxyphthalamidone, $\begin{matrix} C\ H_6\cdot N\cdot CO \\ | \quad\quad | \quad | \\ N\text{——}C\cdot C_6H_2(OMe)_2 \end{matrix}$, is prepared from *αβ-naphthylenamidinedimethoxybenzenylorthocarboxylic acid* [m. p. 242°; from orthonaphthylenediamine (1 mol.) and opianic acid (2 mols.)], and melts at 191—192°.

When nitropianic acid is heated with 1 : 3 : 4-toluylenediamine (2 mols.; opianic acid reacts with 1 mol.), *toluylenaldehydenitrodimethoxybenzenylorthocarboxylic acid*,

$$\begin{matrix} C_6H_3Me\cdot N\cdot CH_2\cdot C_6H(OMe)_2(NO_2)\cdot COOH \\ | \quad\quad\quad | \quad\quad\quad | \\ N\text{———}C\cdot C_6H(OMe)_2(NO_2)\cdot COOH \end{matrix},$$

is formed. Bromopianic acid reacts in like manner with 1 : 3 : 4-toluylenediamine, forming the *acid*

$$\begin{matrix} C_6H_3Me\cdot N\cdot CH_2\cdot C_6HBr(OMe)_2\cdot COOH \\ | \quad\quad\quad | \quad\quad\quad | \\ N\text{———}C\cdot C_6HBr(OMe)_2\cdot COOH \end{matrix},$$

of melting point 213°.

The formation of phthalamidones from the amidinecarboxylic acids is a reversible action, the latter being obtained from the former by the assimilation of a molecule of water. The phthalamidones, moreover, unite with 1 mol. of alcohol; a *compound*, for example, is formed when bromotoluylenephthalamidone is crystallised from alcohol; it melts at 255—256°, and an *isomeride*, melting at 137—138°, is produced by boiling bromotoluylenephthalamidone with alcohol containing a trace of potash; by the latter method also, a *compound* which melts at 163—164° can be obtained from toluylenephthalamidone; and one melting at 173° from toluylenedimethoxyphthalamidone. When zinc-dust is added to hot solutions of phthalamidones, they are decolorised, and ammonia precipitates tetrahydro-derivatives, which are basic substances. Tetrahydrotoluylenephthalamidone melts at 186—187°; whilst tetrahydrotoluylenedimethoxyphthalamidone melts at 248°. A. R. L.

Cinchona Alkaloïds. By A. Claus (*Annalen*, **269**, 232—294). —In this paper, the author gives an account of experiments some of which he and his pupils carried out some years ago, but which have not yet been published in any chemical journal.

Quinidine methiodide, $C_{20}H_{24}N_2O_2,MeI + H_2O$, is formed when quinidine is treated with methyl iodide; it crystallises in lustrous, colourless needles, loses its water at 110°, melts at 248° with decomposition, and is only sparingly soluble in cold water, but readily in alcohol and boiling water. The *ethiodide*, $C_{20}H_{24}N_2O_2,EtI$, crystallises in colourless needles, melts at 248° with decomposition, and is only very sparingly soluble in cold water, but more readily in hot water and alcohol. The *ethobromide*, $C_{20}H_{24}N_2O_2,EtBr + H_2O$, crystallises in long, colourless needles, loses its water at 120°, and melts at about 238° with decomposition.

Methylquinidine, $C_{20}H_{23}N_2O_2Me$, is obtained when the methiodide is boiled with an alkali; it is a yellow oil, readily soluble in ether, chloroform, benzene, and dilute acids. *Ethylquinidine*, $C_{20}H_{23}N_2O_2Et$, prepared in like manner, is a yellow oil.

Quinidine benzyl chloride, $C_{20}H_{24}N_2O_2,C_7H_7Cl$, is a colourless, vitreous compound, melts at 190—195°, and is readily soluble in water and alcohol; its *platinochloride*, $C_{27}H_{31}N_2O_2,HCl,PtCl_4$, is a yellowish-red, crystalline powder.

Quinidine dimethiodide, $C_{20}H_{24}N_2O_2,2MeI + 1\frac{1}{2}H_2O$, crystallises in lemon-yellow, seemingly rhombic plates, loses its water at 130°, begins to decompose at 148°, and melts at 156°; it is more readily soluble in water, but more sparingly in alcohol than the methiodide. The *diethiodide*, $C_{20}H_{24}N_2O_2,2EtI$, crystallises in reddish-yellow prisms with $1\frac{1}{2}$ mols. H_2O or in light yellow plates with 1 mol. H_2O; it begins to decompose at about 170°, melts at 205°, and is very readily soluble in hot water, but much more sparingly in alcohol.

Quinidine diethyl nitrate, $C_{90}H_{24}N_2O_2,2EtNO_3 + H_2O$, prepared by warming an aqueous solution of the diethiodide with silver nitrate, crystallises in large, transparent prisms, loses its water over sulphuric acid, and melts at 91° with decomposition. The corresponding *sulphate*, $C_{20}H_{24}N_2O_2,Et_2SO_4$, is a brown syrup.

Ethylchitenidine, $C_{19}H_{21}EtN_2O_4$, can be obtained by oxidising quinidineethylammonium hydroxide with potassium permanganate in the cold; it crystallises in well-defined, yellowish prisms containing 3 to 4 mols. H_2O, loses its water at 100°, melts at 287°, and is readily soluble in hot water, dilute alcohol, acids, and dilute alkalis, but insoluble in ether. The *platinochloride*, $C_{19}H_{21}EtN_2O_4,H_2PtCl_6$, is a yellow, crystalline compound, and seems to contain 2 mols. H_2O. The *sulphate*, $C_{19}H_{21}EtN_2O_4,H_2SO_4$, crystallises in small prisms, and melts at 218° with decomposition.

Benzyldihydroxycinchotenine, $C_{18}H_{19}N_2O_5{\cdot}C_7H_7$, is formed when cinchonine benzyl chloride is oxidised with potassium permanganate in the cold. It crystallises in slender, colourless needles, melts at 278° with decomposition, and is almost insoluble in water, cold alcohol, ether, and chloroform, but soluble in hot alcohol and acids. The *hydrochloride*, $C_{25}H_{26}N_2O_5,2HCl + H_2O$, crystallises from hot water in lustrous, efflorescent needles. The *platinochloride*, $C_{25}H_{26}N_2O_5,H_2PtCl_6$, separates from hot alcohol in yellowish-red crystals, melts at 290—291° with decomposition, and is insoluble in water. The *mercurochloride*, $C_{25}H_{26}N_2O_5,H_2HgCl_4$, forms small, colourless needles. The *sulphate*, $C_{25}H_{26}N_2O_5,H_2SO_4$, separates from dilute alcohol in lustrous, efflorescent needles. The *nitrate*, $C_{25}H_{26}N_2O_5,HNO_3 + 2H_2O$, crystallises in needles, loses its water at 100°, and melts at 178°. The *dimethiodide*, $C_{25}H_{26}N_2O_5,2MeI$, crystallises from alcohol in yellow needles, and melts at 205° with decomposition; it separates from water in yellowish-brown, prismatic crystals which contain $3\frac{1}{2}$ mols. H_2O, and melt at 198° with decomposition. The *dimethobromide*,

$$C_{25}H_{26}N_2O_5,2MeBr,$$

forms yellow needles, melts at 210° with decomposition, and dissolves freely in water and alcohol.

Benzyldihydroxycinchotenidine, $C_{18}H_{19}N_2O_5 \cdot C_7H_7$, can be obtained by oxidising cinchonidine benzyl chloride with potassium permanganate. It crystallises in slender, colourless needles, melts at 248°, and is readily soluble in hot alcohol and dilute acids, but only very sparingly in hot water, and insoluble in ether and chloroform. The *platinochloride*, $C_{25}H_{26}N_2O_5,H_2PtCl_6$, is a heavy, yellow, crystalline powder. The *mercurochloride*, $C_{25}H_{26}N_2O_5,H_2HgCl_4$, separates from hot alcohol in slender, colourless needles.

Cinchonidine benzyl chloride, $C_{19}H_{22}N_2O,C_7H_7Cl + H_2O$, crystallises from water in large octahedra, loses its water at 100°, and melts at 198° with decomposition; it is only very sparingly soluble in cold water, but dissolves freely in alcohol, acids, and hot water. The *platinochloride*, $C_{26}H_{29}N_2ClO,HCl,PtCl_4 + H_2O$, is a yellow, crystalline powder insoluble in water and alcohol. The *mercurochloride*, $C_{26}H_{29}N_2ClO,HCl,HgCl_2$, crystallises from boiling alcohol in lustrous needles, and is only sparingly soluble in cold water.

Benylcinchonidine, $C_{19}H_{21}N_2O \cdot C_7H_7$, prepared by treating the preceding compound with potash, is a yellow oil. The *platinochloride*, $C_{26}H_{28}N_2O,H_2PtCl_6 + 3H_2O$, is a yellow, crystalline compound, and loses its water at 110°.

The following experiments show that when cinchonidine is caused to combine both with 1 mol. of methyl iodide and 1 mol. of ethyl iodide, the properties of the final product are dependent on the order in which combination has taken place.

Cinchonidine methiodide hydriodide, $C_{19}H_{22}N_2O,MeI,HI + H_2O$, is obtained by the action of ethyl iodide on cinchonidine methiodide in alcoholic solution; it crystallises from water in pale yellow, monosymmetric prisms, $a : b : c = 0{\cdot}3440 : 1 : 0{\cdot}3048$, $\beta = 77°\ 57'$, loses its water at 105°, and melts at 240—242° with decomposition.

Cinchonidine dimethiodide, $C_{19}H_{22}N_2O,2MeI + 2H_2O$, crystallises from water in reddish, rhombic prisms, $a : b : c = 0{\cdot}5033 : 1 : 0{\cdot}3140$.

Cinchonidine methiodide ethiodide, $C_{19}H_{22}N_2O,MeI,EtI + 2H_2O$, prepared by heating the methiodide with ethyl iodide in alcoholic solution at 120—150°, separates from water and from alcohol in reddish-yellow, rhombic crystals, $a : b : c = 0{\cdot}6992 : 1 : 0{\cdot}9662$, loses its water at 105°, and melts at 243—245° with decomposition.

Cinchonidine ethiodide hydriodide, $C_{19}H_{22}N_2O,EtI,HI + H_2O$, forms monosymmetric crystals, $a : b : c = 1{\cdot}0849 : 1 : 1{\cdot}6775$, $\beta = 78°\ 39'$, loses its water at about 105°, and melts at 225° with previous decomposition.

Cinchonidine ethiodide methiodide, $C_{19}H_{22}N_2O,EtI,MeI$, prepared by treating the ethiodide with methyl iodide, forms yellow, monosymmetric crystals, $a : b : c = 1{\cdot}6304 : 1 : 1{\cdot}0190$, $\beta = 81°\ 39'$, and melts at 255° with decomposition.

Cinchonidine diethiodide, $C_{19}H_{22}N_2O,2EtI$, forms anhydrous, rhombic plates, $a : b : c = 1{\cdot}5527 : 1 : 1{\cdot}0408$, and long, rhombic prisms, $a : b : c = 0{\cdot}7341 : 1 : 0{\cdot}9557$, which contain 2 mols. H_2O.

Cinchonine ethocyanide, $C_{19}H_{22}N_2O,EtCN$, prepared by treating cinchonine ethyl sulphate with barium cyanide, crystallises in colourless needles or prisms, melts at 160—165° with decomposition, and is readily soluble in water and alcohol, but insoluble in ether.

A compound of the composition $C_{19}H_{22}N_2O,EtI,Hg(CN)_2$ is precipitated in colourless crystals when a solution of cinchonine ethyl iodide is treated with mercuric cyanide; it melts at 210° with decomposition, and is soluble in hot water and alcohol, but insoluble in ether. The corresponding *bromide*, $C_{19}H_{22}N_2O,EtBr,Hg(CN)_2$, crystallises from alcohol in colourless needles, melts at 200° with decomposition, and is soluble in boiling water. The compound of the composition $C_{19}H_{22}N_2O,C_7H_7Cl,Hg(CN)_2$ crystallises from alcohol in colourless prisms, and melts at 220° with decomposition.

A compound of the composition $C_{19}H_{22}N_2O,EtI,AgCN$ is formed when cinchonine ethiodide is treated with silver cyanide; it crystallises in needles, and melts at 195°. The corresponding *bromide*, $C_{19}H_{22}N_2O,EtBr,AgCN$, forms small, colourless needles, and melts at 194° with decomposition.

Cinchonine diethyl nitrate, $C_{19}H_{22}N_2O,2EtNO_3$, prepared by decomposing the diethiodide with silver nitrate, crystallises from water in transparent plates, and melts at 245° with decomposition. The corresponding *sulphate*, $C_{19}H_{22}N_2O,Et_2SO_4 + 2H_2O$, forms yellowish needles, and melts at 208° with decomposition. The corresponding *chloride*, $C_{19}H_{22}N_2O,2EtCl + 2H_2O$, is a crystalline, hygroscopic compound, and melts at 205° with decomposition.

A compound of the composition $C_{19}H_{22}N_2O,2EtI,2Hg(CN)_2$ is formed when a concentrated solution of cinchonine diethiodide is treated with mercuric cyanide; it separates from boiling alcohol as a powder, begins to decompose at 120°, and melts at 155°. The corresponding *bromide*, $C_{19}H_{22}N_2O,2EtBr,2Hg(CN)_2$, is a colourless, crystalline powder, and melts at 180° with decomposition.

The above experiments, and the results of a comparative study of the alkyl halogen additive products of isoquinoline, pyridine, and the cinchona alkaloïds which the author and his pupils have previously published, lead to the conclusion that in the cinchona alkaloïds the nitrogen atom with which the first added alkyl halogen molecule combines is analogous in function, and is combined in the same way as the nitrogen atoms in isoquinoline and in pyridine respectively; the nitrogen atom with which the second added alkyl halogen molecule combines has, on the other hand, the same function as the nitrogen atom in quinoline.

Diethylidenecinchonine, $C_{23}H_{30}N_2O$, is obtained by treating the dialkyl halogen additive products of cinchonine with moderately concentrated alkalis; it is a yellow powder, melts at about 85°, turns red on exposure to the air, and is very readily soluble in alcohol and dilute acids, but only sparingly in water. The *platinochloride* $C_{23}H_{30}N_2O,H_2PtCl_6$ is a yellow, crystalline powder. The *ethobromide* $C_{23}H_{30}N_2O,EtBr$, obtained by heating the base with ethyl bromide at 100°, is a reddish-brown, amorphous substance. The *methiodide*, $C_{23}H_{30}N_2O,MeI$, is a yellowish-red powder, soluble in water and alcohol.

Triethylidenecinchonine, $C_{25}H_{34}N_2O$, is formed when the ethobromide just described is boiled for a long time with potash; it is a reddish-brown, resinous substance.

Diethylidenecinchoxine, $(C_{23}H_{30}N_2O)_2O$, is formed when diethylidene-

cinchonine undergoes oxidation by exposure to the air; it is a dark-red powder, melts at 95°, and dissolves freely in dilute acids. The *platinochloride*, $(C_{23}H_{30}N_2O)_2O,H_2PtCl_6$, is a heavy, reddish-yellow powder. The *ethobromide*, $(C_{23}H_{30}N_2O)_2O,2EtBr$, is a brown syrup.

F. S. K.

Bases Homologous with Quinine. By E. Grimaux and A. Arnaud (*Compt. rend.*, **114**, 672—673).—Cupreïne, $C_{19}H_{21}N_2O{\cdot}OH$ (Abstr., 1891, 1121), is the hydroxy-compound of which quinine and quinethyline are the corresponding methoxy- and ethoxy-compounds. The authors have now prepared quinopropyline, quinisopropyline, and quinamyline.

Quinopropyline, $C_{19}H_{21}N_2O{\cdot}OPr^{\alpha}$, is prepared by heating sodium cupreïne (3·2 grams of cupreïne, 0·35 gram of sodium) with propyl nitrate (1·6 grams) and propyl alcohol (50 c.c.) at 110° for 24 hours. The free base, which is precipitated as a hydrate on the addition of ammonia to the aqueous solution of the basic sulphate, melts at 100° in the hydrated condition, but at 164° after drying in a vacuum. It may be obtained in long needles by slow evaporation of its solution in dilute ammonia saturated with ether. The *basic sulphate*,

$$(C_{22}H_{25}N_2O_2)_2,H_2SO_4,1\tfrac{1}{2}H_2O,$$

crystallises from boiling solutions in silky, micaceous needles, from moderately dilute solutions in gelatinous agglomerates, and from cold solutions in large, single needles. It melts at 223—224°, and dissolves in 454 parts of water at 13°. Its specific rotatory power at 22° is $[\alpha]_D = +229{\cdot}5°$.

Quinisopropyline is prepared in the same way. The free base melts at 154°. The *basic sulphate*, $(C_{22}H_{28}N_2O_2)_2,H_2SO_4,H_2O$, crystallises from boiling solutions in colourless needles, but from cold solutions in small, kidney-shaped crystals aggregated into a horny mass. It dissolves in 367 parts of water at 10°, and has a rotatory power of $[\alpha]_D = +229{\cdot}2°$ at 22°.

Quinamyline is prepared by heating amyl chloride with a solution of sodium cupreïne in amyl alcohol at 105° for 15 hours. The crude product is treated with soda and shaken with ether, and the ethereal solution treated with very dilute sulphuric acid; alcohol is then added to the warm acid solution, and it is neutralised with ammonia. On concentration, the basic sulphate crystallises out and may be recrystallised from alcohol. The pure base is amorphous, and melts at 166·5—167°. Its solution in dilute sulphuric acid is fluorescent. The *normal sulphate* is amorphous. The *basic sulphate*,

$$(C_{24}H_{32}N_2O_2)_2,H_2SO_4,2H_2O,$$

crystallises in long needles on cooling its alcoholic solution. It is very soluble in alcohol, less so in water (1 in 4170 at 11·5°).

Jn. W.

Apocinchonine and Diapocinchonine. By E. Jungfleisch and E. Leger (*Compt. rend.*, **114**, 1192—1195).—The apocinchonine formed by the action of dilute sulphuric acid on cinchonine (*Compt. rend.*, **113**, 653) exists in that part of the product which is insoluble in ether and in dilute alcohol. This mixture is treated with strong

boiling alcohol, and after separation of the greater part of the cinchoniline and cinchonifine by fractional crystallisation, the mother liquor is mixed with a small quantity of alcohol and then diluted with its own volume of water. The apocinchonine separates and may be recrystallised from strong alcohol; the oxycinchonines and other bases remain in solution. Further purification of the apocinchonine is effected by converting it into oxalate, which readily crystallises. It is identical with the apocinchonine obtained from cinchonine by the action of hydrochloric acid, but the action of sulphuric acid gives a much lower yield. No trace of the α- and β-oxycinchonines is found in the product of the action of hydrochloric acid, and their formation under the influence of sulphuric acid is most probably due to the intermediate formation of sulphonic derivatives, or some other specific action of the acid. It is clear that the oxycinchonines do not exist, as Hesse suggested, as impurities in the original cinchonine.

The diapocinchonine, stated by Hesse to exist in the alcoholic mother liquor from apocinchonine, is a mixture of cinchoniline and cinchonigine with another base not yet isolated. C. H. B.

Aconitine. By A. Ehrenberg and C. Purfürst (*J. pr. Chem.* [2], **45**, 604—613).—The aconitine was purified from a large commercial sample by recrystallisation from ether, only the middle fraction being used. The pure alkaloïd melts at 193—194° (compare Dunstan and Ince, Trans., 1891, 271), but the presence of a very small quantity of a decomposition product, which coats the crystals like a varnish and therefore escapes detection, lowers the melting point by 10° and more; for this reason the purification of aconitine by converting it into a salt and decomposing this by an alkali is inadmissible. The authors' formula for aconitine is $C_{32}H_{43}NO_{11}$; Wright and Luff give $C_{33}H_{43}NO_{12}$ (Trans., 1878, 152); Dunstan and Umney, $C_{33}H_{45}NO_{12}$ (*loc. cit.*; compare, however, Trans., 1892, 391). Determinations of methoxyl by Zeisel's method showed 9·92, 9·98, and 10·13 per cent. of methyl as methoxyl; the elimination of four methyl groups from the above formula would give 9·73 per cent.

When hydrolysed by alcoholic potash, or by water, at 140—150°, aconitine yields a new base, methyl alcohol, benzoic acid, and another acid (compare authors quoted). When it is heated with water in a reflux apparatus until it has all dissolved, picroaconitine and napelline are produced, and crystallise from the solution as benzoates; they may be approximately separated by treatment with dilute sulphuric acid, washing with ether to extract the liberated benzoic acid, adding sodium carbonate until there is a slight precipitate and again shaking with ether, which extracts the napelline; the picroaconitine is obtained by digesting the slightly alkaline solid residue with ether. The picroaconitine, $C_{25}H_{39}NO_{11}$, is probably formed from 1 mol. of aconitine by the absorption of 1 mol. of water and elimination of 1 mol. of benzoic acid, and the napelline, $C_{24}H_{37}NO_{10}$, from 1 mol. of picroaconitine, by the absorption of 1 mol. of water and elimination of 1 mol. of methyl alcohol. The mother liquors from the picroaconitine and napelline benzoates contain aconine, $C_{22}H_{35}NO_9$, and acetic acid; this points to the formation of 1 mol. of aconine from 1 mol. of

napelline by the absorption of 1 mol. of water and elimination of 1 mol. of acetic acid.

When aconine is distilled with barium hydroxide, paraffin hydrocarbons, methylamine, and an oily compound which boils at about 245° and has an odour of quinoline are obtained. This matter is being further investigated.

The so-called amorphous aconitine of commerce is a variable mixture of aconitine, picroaconitine, and napelline. A. G. B.

Scopolamine (Hyoscine). By E. Schmidt (*Arch. Pharm.*, **230**, 207—231; compare Abstr., 1891, 228).—Inasmuch as the name hyoscine has been misapplied to tropine, it has become somewhat ambiguous, and the author proposes to call the hyoscine from hyoscyamus, *scopolamine*, a name which is in accord with the recent isolation of this alkaloid from *Scopolia atropoïdes* (Abstr., 1890, 658).

Scopolamine, $C_{17}H_{21}NO_4 + H_2O$, crystallises well, and melts at 59° to a colourless liquid, which does not crystallise again. The aurochloride crystallises in needles, and melts at 212—214° (uncorr.), not 198° (Ladenburg, Abstr., 1881, 446), although a small quantity of an aurochloride, having the latter melting point, was obtained (compare Abstr., 1888, 856). The hydrobromide crystallises with 3 mols. H_2O, and the hydrochloride with 2 mols. H_2O, whilst the hydriodide and sulphate are anhydrous. The *acetyl* derivative was prepared, and its *aurochloride*, $C_{17}H_{20}AcNO_4,HAuCl_4$, was crystallised; the presence of a hydroxyl group is thus indicated. Nitrous acid has practically no action on scopolamine, which may, therefore, be regarded as a tertiary base. When boiled with baryta-water, scopolamine is split up into atropic acid and a base which the author designates scopoline, $C_8H_{13}NO_2$. This base boils at 241—243° (uncorr.) and melts at 110°; its aurochloride melts at 223—225°, and its platinochloride at 228—230°. The identity of scopoline is somewhat uncertain; its boiling point agrees with that of oxytropine (Abstr., 1884, 761); it also agrees in the temperature constants of itself and salts, but not in formula, with pseudotropine (Abstr., 1884, 761; 1891, 1265; this vol., 891). The isomerism of scopolamine with cocaïne is to be noted.

Scopolamine was also obtained from *Hyoscyamus niger*, *Atropa belladonna*, *Datura stramonium*, and *Duboisia myoporoïdes*.

A. G. B.

Subsidiary Alkaloïds of Belladonna. By E. Merck (*Arch. Pharm.*, **230**, 134—141).—According to our present knowledge, crude belladonine (the mother liquor from atropine crystallisation) contains atropamine, belladonine, and hyoscine, their decomposition products, tropine and pseudotropine, and the derivatives of these, atropic and isatropic acids. The more recent work on the subject will be found in Abstr., 1884, 761, 1055; 1890, 271; 1891, 228, 748.

Apoatropine was first prepared by Pesci (Abstr., 1882, 740). Its *hydrochloride*, $C_{17}H_{21}NO_2,HCl$, forms white, lustrous, anhydrous laminæ, which melt at 237—239°, and dissolve sparingly in cold water. The *hydrobromide* crystallises in long needles and lustrous,

white laminæ, and melts at 230°. The *hydriodide* forms small, white needles. The *aurochloride*, $C_{17}H_{21}NO_2,HAuCl_4$, crystallises in long, slender, yellow needles, dissolves sparingly in cold water, and melts at 110—111°. The *platinochloride*, $(C_{17}H_{21}NO_2)_2,H_2PtCl_6$, melts at 212—214° with decomposition. The *mercurochloride*,

$$C_{17}H_{21}NO_2,HHgCl_3,$$

stannochloride, *chromate*, and *picrate* (m. p. 166—168°) were also prepared. A comparison of these salts with those of Hesse's atropamine (Abstr., 1891, 228) leads to the conclusion that this base is identical with apoatropine; Hesse, however, did not crystallise atropamine.

Apoatropine was decomposed by alcoholic potassium hydroxide, and the basic products extracted with chloroform, leaving the acids to be extracted with ether after acidification. The chloroform solution having been dried over potassium carbonate and evaporated, left a base which boiled at 227—229° and solidified on cooling to a white, crystalline mass; the platinochloride melted at 201° with decomposition, and the aurochloride at 206°. These properties correspond with those of tropine. Hesse (*loc. cit.*) described the product of the decomposition of atropamine by alkalis as pseudotropine, but it is not identical with the pseudotropine obtained from hyoscine. The ethereal extract of the acidified decomposition product contained atropic acid. The author comes to the conclusion that apoatropine is identical with atropamine, and that Hesse's base (b. p. 242°) is pseudotropine. A. G. B.

Chlorocruorine. By A. B. Griffiths (*Compt. rend.*, **114**, 1277—1278).—Chlorocruorine exists in two states, namely, oxychlorocruorine, which shows absorption bands at λ 618—593 and at λ 576—554·5, and reduced or ordinary chlorocruorine, which shows a single badly defined band between C and D.

Chlorocruorine extracted by the method previously described (*Compt. rend.*, **114**, 840) has the composition

C.	H.	N.	Fe.	S.	O.	
54·23	6·82	16·16	0·45	0·78	21·56	= 100,

which corresponds with the formula $C_{560}H_{845}N_{143}FeS_3O_{167}$. When treated with acids and alkalis, it yields hæmatin, a proteïd, and fatty acids.

The ash of the blood of *Sabella* has the composition

Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	SO_3.	Cl.	
0·18	3·42	1·22	4·03	45·23	4·56	2·10	39·26	= 100·00

C. H. B.

Physiological Chemistry.

Respiration Apparatus. By J. Haldane (*J. Physiol.*, **13**, 419—430).—A simple and effective apparatus for measuring the respiratory exchange of small animals is described. It consists of five Woulff's bottles; between the second and third the animal chamber is placed; the series is connected by glass and india-rubber tubing. Air is drawn through the apparatus by a filter pump; a meter measuring the rate of ventilation. The first bottle is filled with soda-lime, the second with sulphuric acid and pumice stone. These deprive the atmospheric air of carbonic anhydride and moisture respectively. Bottles 3 and 5 are also filled with pumice stone and sulphuric acid; bottle 4, with soda-lime. Bottles 3, and 4 and 5 together, are weighed before and after the experiment. The increase of weight gives the moisture and carbonic anhydride produced by the animal. The absorption is very complete even with rapid ventilation (1 to 7 litres of air per minute). The oxygen absorbed is measured by the difference in the increase of weight of bottles 3, 4, and 5, and the loss of weight of the animal chamber with the animal within it.

For human beings Pettenkofer's apparatus is more convenient. It may, however, be much simplified by using soda-lime instead of baryta-water. W. D. H.

Formation of Uric Acid in Mammals. By F. Mares (*Monatsh.*, **13**, 101—110).—The author has previously (*Archives slaves de Biologie*, **3**, 207) advanced the view that uric acid is a product of change occurring within the living cell, but had not then determined which of the substances present in the cell gives rise to the acid. Horbaczewski (Abstr., 1891, 1340) has referred the formation of the acid to the nucleïn of the cell; and our present knowledge of the origin of the acid may be accordingly formulated:—"Uric acid is a product of metabolism occurring within the living cells of mammals, in the formation of which the nucleïn of the cell-nuclei is specially concerned." G. T. M.

Dissolved Nitrogen in Blood. By F. Jolyet and C. Sigalas (*Compt. rend.*, **114**, 686—688).—Parallel series of estimations of the volumes of nitrogen and hydrogen absorbed by blood of varying degrees of richness, with whole corpuscles, with broken up corpuscles, and with serum alone, show that the absorption of both these gases increases with the number of corpuscles, and is greatly diminished by breaking them up, and that the amount of nitrogen absorbed is always greater in corresponding experiments than the amount of hydrogen. It is, therefore, probable that the gases form a layer on the surface of the corpuscles, and this view is borne out by the well known fact that hydrogen adheres much less readily than any other gas to surfaces. Jn. W.

Absorption of Water from the Alimentary Canal. By J. S. Edkins (*J. Physiol.*, **13**, 445—459).—The animal (cat) is anæsthetised by morphine, and atropine injected subcutaneously, *plus* chloroform. A length of alimentary canal is tied off from the rest, cleaned, and normal saline solution introduced from a burette at constant pressure. The amount of secretion from the gastric and intestinal wall is small, and may be disregarded. A little mucus is generally found. The difference between the amount of liquid used, and the amount recovered at the end of the experiment, which always lasts one hour, gives the amount absorbed. This, divided by the length of the ligatured portion of the canal, gives the "coefficient of absorption," that is, the amount absorbed per centimetre per hour at the given pressure. A pressure of 10 cm. was usually employed.

The results obtained were the following:—

1. The absorption in the large intestine is considerable, the average coefficient of absorption being 2·07 c.c.

2. In the ileum, the coefficient of absorption is less constant, and averages 1·31 c.c.

3. In the jejunum it is 0·727 c.c.

4. In the stomach, whatever state of digestion it was in, the coefficient is practically nothing. W. D. H.

Ptomaïnes of Infectious Diseases. By A. B. Griffiths (*Compt. rend.*, **114**, 1382—1384).—*Glanders.*—The author has extracted from the urine of victims to glanders a ptomaïne which forms white crystals of the composition $C_{15}H_{10}N_2O_6$. The hydrochloride, platinochloride, and aurochloride are all crystalline. Its solutions give a greenish precipitate with phosphotungstic acid, a brownish-white precipitate with phosphomolybdic acid, a yellow precipitate with picric acid, and a precipitate with Nessler's solution. The base is poisonous, and when injected under the skin of a rabbit, produces abscesses at the point of injection, peculiar nodular lesions in the lungs, &c., and finally, death.

Pneumonia.—The ptomaïne from the urine of pneumonia patients forms white, microscopic needles, soluble in water, forming an alkaline solution. It forms a hydrochloride, platinochloride, and aurochloride, and its solutions give a white precipitate with phosphotungstic acid, a yellowish-white precipitate with phosphomolybdic acid, a yellow precipitate with picric acid, and a brownish precipitate with Nessler's solution. The base has the composition $C_{20}H_{26}N_2O_3$, and its specific rotatory power is $[\alpha]_D = +23·5°$.

Neither of these ptomaïnes is found in normal urine.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Aërobic Nitrate-reducing Ferment in Straw. By E. Bréal (*Compt. rend.*, **114**, 681—684).—Straw always contains nitrates on its surface, as shown by the diphenylamine reaction, but after soaking in water for a few days, the nitrates disappear, and increasing quantities then added to the water also disappear. This action is due to a ferment, for if the straw is previously sterilised it does not take place, and the ferment is aërobic, for the action soon stops in the absence of air. The nitrates are reduced partly to free nitrogen, which can be collected and examined, and partly to nitrogen in organic combination. The reduction is not to be feared in ordinary humus soils, as the amount of water they contain is insufficient for the growth of the ferment, but in prairie and forest soils it probably forms an important factor in the cycle of change. Jn. W.

Respiration of Plants under Lessened Oxygen Tension, and when Injured. By Stich (*Bied. Centr.*, **21**, 350; from *Sitzungsber. Wien. Akad.*, 1890, 407).—The normal respiration and production of carbonic anhydride in hydrogen were determined, that is, by intramolecular respiration with complete exclusion of oxygen. The addition of 20·8, 8, 6, 4, 2, and 0 per cent. of oxygen showed the independence of the production of carbonic anhydride on the presence of atmospheric oxygen in rather wide limits, there being no striking diminution with 4 to 2 per cent. of oxygen. In the case of many objects, as, for instance, the fruits of *Jasminum fructicans* and *Sambucus nigra*, and the seedlings of *Ricinus communis*, *Vicia faba*, and *Lupinus albus*, the production of carbonic anhydride was not influenced by the amount of oxygen present, and was as great in an atmosphere of hydrogen as in air. The relation of the carbonic anhydride which was found to the oxygen taken up was not altered when 8 per cent. of oxygen was present, and when the experiment lasted from 3 to 24 hours. With 3—4 per cent. the quotient $CO_2 : O$ was altered in favour of CO_2.

Experiments were made with a large number of plants to ascertain the effect of injury (from scratches to complete cutting up) on respiration. An increased separation of carbonic anhydride was always noticed; but the various plants and parts of plants behaved differently with regard to the extent and duration of the increase.

N. H. M.

Nutrition of Green Plant Cells with Formaldehyde. By T. Bokorny (*Landw. Jahrb.*, **21**, 445—465).—The artificial nutrition of green plant cells has been successfully accomplished by several investigators. Böhn (*Bot. Zeit.*, 1883) showed that some leaves, freed from starch, produced starch in a few days when placed on a solution of sugar. Similar results were obtained by Klebs (*Ber. deut. bot. Ges.*, **5**, 186), A. Meyer (*Bot. Zeit.*, 1885), and E. Laurent. Both Meyer and Laurent proved that mannitol and dulcitol will give rise to starch production, whilst with erythritol they obtained negative

results. They also showed (almost contemporaneously, *Bot. Zeit.*, 1886, 81) that glycerol is a starch-forming substance; this was also observed by the author, who further showed that ethylidene glycol and methyl alcohol have the same property (*Landw. Versuchs-Stat.*, 1889, 235). According to v. Baeyer's hypothesis, formaldehyde is an intermediate product in the production of carbohydrates from carbonic anhydride; the object of the experiments described in the present paper was to ascertain whether plant cells could produce starch when supplied with formaldehyde instead of carbonic anhydride. It has not yet been shown that formaldehyde even exists in plants. Owing to its poisonous nature and its great instability, it is unlikely that it occurs in sufficient amount to be detected (compare Reinke, *Ber. deut. bot. Ges.*, **14**, 2150).

In order to obtain plants free from starch, nutritive solutions free from potash were employed—potash being necessary, as Nobbe has shown, for starch production—whilst the already formed starch was eliminated by adding an excess of nitrate to the nutritive solution. In this manner it was possible to obtain Spirogyræ, free from starch, in a few days, even in full daylight. To prevent assimilation of carbonic anhydride during the experiment there are three methods: (1) keeping the plants in the dark, (2) employing an atmosphere free from carbonic anhydride, and (3) the omission of potassium from the nutritive solution. The first of these methods is, however, not always applicable in these experiments, as many of the organic substances are only assimilated in presence of light.

The organic compounds experimented with have to be employed in such amounts as are without injury to the plants. Solutions of methyl alcohol must not be stronger than 0·5 per cent.; sugar solutions may be employed, which contain as much as 10 to 20 per cent., whilst formaldehyde had to be diluted to 1 : 50,000 in order to keep the Spirogyræ alive for a few days; in fact, experiments with free formaldehyde had to be discontinued. Satisfactory results were, however, obtained with the double compound of formaldehyde with sodium hydrogen sulphite, which has already been employed by O. Loew in his experiments with fungi (*Bot. Centr.*, 1890). When the double compound is used, it is necessary to add some disodium hydrogen phosphate to the nutritive solution in order to convert the hydrogen sodium sulphite, when liberated, into the disodium salt. Care must also be taken to select a suitable plant: many plants are injured by the dialkali phosphate, whilst others decompose the formaldehyde too quickly, &c.

Satisfactory results were obtained with a small variety of Spirogyræ (*flavescens?*), with *S. majuscula*, and with *S. nitida*. When exposed to light, there was considerable production of starch from formaldehyde in absence of carbonic anhydride, whilst experiments without formaldehyde showed no formation of starch. The results were confirmed by quantitative experiments, in which weighed amounts of Spirogyræ were shown to gain considerably in dry substance, and to form very large amounts of starch. Thus, an amount of *S. nitida* containing 0·21 gram of dry matter, grown in a solution containing sodium formaldehyde sulphite (0·1), disodium phosphate

(0·05), calcium nitrite (0·1), magnesium sulphite (0·025), and calcium chloride (0·05 per cent.), contained, after 10 days, 0·26 gram of dry matter, excluding portions which died during the experiment. A control experiment, without formaldehyde, showed that no starch was formed, and that there was no increase of dry matter. Other experiments gave similar results. Experiments were then made to ascertain the loss of formaldehyde which takes place: in a check experiment, without the plants, there was no loss, whilst with plants 145·8 milligrams (out of 250 milligrams) disappeared in 10 days.

Zygnema cruciatum.—A quantity of *Zygnema*, poor in starch, was put into a 250 c.c. stoppered flask containing the mineral nutritive solution with 0·2 per cent. of sodium formaldehyde sulphite. The algæ grew well, and formed considerable amounts of starch; they remained quite healthy, and no threads died in eight days. The experiment was repeated in a closed space, kept free from carbonic anhydride by means of potash, the nutritive solutions being kept in glass dishes. When formaldehyde was withheld, the algæ remained poor in starch, whilst in presence of formaldehyde there was a very great production of starch. Neither fungi nor infusoriæ were found, so that there can have been no evolution of carbonic anhydride.

The results of the experiments show that green plant cells have the power of decomposing sodium formaldehyde sulphite and immediately condensing the formaldehyde liberated. Light plays an important part in the synthesis, and in a feeble light the starch formation is very slow, whilst in absence of light no carbohydrate is produced. Under the influence of light and formaldehyde, the plants gain considerably in dry matter in absence of carbonic anhydride.

N. H. M.

Fat-decomposing Ferments in Plants. By W. Sigmund (*Bied. Centr.*, **21**, 350; from *Sitzungsber. Wien. Akad.*, 1890, 407, and 1891, 328).—The experiments were made with oily seeds, chiefly rape. The ferments soluble in water and glycerol, but insoluble in alcohol, were dried at 30° and mixed to an emulsion with weighed amounts of fatty oils. In 24 hours, titration with decinormal alkali showed a distinct increase of free acid. The action of the ferment is of similar (less) intensity to that of the pancreas ferment. Subsequent experiments showed that the co-operation of an organised ferment in the decomposition of the oil is not possible, and the ferment of the seeds showed the characteristic property of all enzymes, being when dry soluble at 100°, but when damp it loses its activity at 80°, so that heated dry seeds gave active, boiled seeds inactive, extracts. Experiments with germinating seeds gave similar results, except that the increase of acid was considerably greater, and that the ferment of the germinated seeds seemed to be more sensitive to heat in the dry state. The ferment has also the power of decomposing alkyl salts, as, for instance, spermaceti, which do not, like glycerides, belong to fats in the narrower sense.

N. H. M.

Influence of Phosphoric Acid on the Formation of Chlorophyll. By O. Löw (*Forsch. a. d. Gebiete d. Agrik.-physik.* **15**, 100; from *Bot. Zentralbl.*, **48**, 371).—Threads of *Spirogyra majuscula* kept

in a solution containing calcium nitrate (0·02) and ammonium sulphate (0·002 per cent.) lived for weeks in diffused daylight. The cells grew, but the increase of the mass seemed very slight. The chlorophyll band was pale-yellow, but was still active, although much less so than under normal conditions. Iron sulphate (0·002 per cent.) was added without any result, but the further addition of disodium phosphate (0·08 per cent.) caused greenness. No unhealthy appearance was observed, owing to the absence of potassium and magnesium. The results support the view that phosphoric acid is necessary as well as iron for the production of a normal chlorophyll. N. H. M.

Origin of the Colouring Matters of the Vine. By A. Gautier (*Compt. rend.*, **114**, 623—629).—See this vol., p. 1242.

The Constituents of Menyanthes trifoliata and of Erythræa centaurium. By K. Lendrich (*Arch. Pharm.*, **230**, 38—60).—To isolate menyanthin from the ethereal extract of *Menyanthes trifoliata*, the ether is evaporated, the residue extracted with water, and the aqueous solution shaken with moist aluminium hydroxide to eliminate tannin; it is then evaporated in a vacuum, the residue treated with absolute alcohol, the solution filtered, distilled to a small volume, mixed with ether, and again filtered; the ether is evaporated, the alcoholic residue boiled with animal charcoal in a reflux apparatus, and finally evaporated in a current of carbonic anhydride. Directions are also given for the isolation of menyanthin from an alcoholic extract of the plant.

Menyanthin, $C_{33}H_{50}O_{14}$, as first obtained is a yellow substance having the consistency of turpentine, a neutral reaction, and bitter taste; when dried in an atmosphere of hydrogen in a current of steam, it becomes solid, and has a glassy fracture. Its aqueous solution gives the following precipitates:—yellow with potassium bismuthoiodide, white with potassium mercuric iodide, yellow with sodium phosphomolybdate, white with tannin, yellow with iodine solution; gold chloride and Fehling's solution are reduced by it. Hot lime-water and baryta-water decompose the aqueous solution. Picric and oxalic acids are among the products of the decomposition of menyanthin by nitric acid, and phenol-like substances are to be detected when it is melted with potassium hydroxide.

The menyanthol obtained by distilling menyanthin with dilute sulphuric acid is a yellow oil with a characteristic odour, but unlike that of benzaldehyde. It has an acid reaction, and in some respects behaves both as an aldehyde and as a phenol; on this account alone, Kromayer's formula, C_8H_8O, for this substance is probably incorrect, and the author's analyses show that $C_7H_{11}O_2$ is the most likely empirical formula. The sugar which is formed when it is decomposed by dilute sulphuric acid is lævorotatory.

Erythrocentaurin, $C_9H_{14}O_6$, is isolated from *Erythræa centaurium* by the same method as that adopted for menyanthin. It is nearly colourless, turpentine-like, bitter, and neutral; it will not crystallise, but dries up, resembling menyanthin in this respect, as also in its solubility and reactions. When distilled with dilute sulphuric acid, it

yields resinous matters, a substance which is both aldehydic and phenolic in properties, and a sugar.

For the investigation of the fatty matters in *Menyanthes trifoliata*, the ether extract from which the menyanthin has been dissolved by water is saponified and extracted by ether, the ether evaporated, and the residue treated with acetone; in this way, ceryl alcohol and a cholesterol can be isolated, whilst formic, acetic, and butyric acids are found in the mass of alkaline salts produced by the saponification. Palmitic acid was also detected, but neither oleïc acid nor glycerol. A red colouring matter is left in the acetone solution after the cholesterol has been separated; it may be purified by evaporating the acetone and extracting with methyl alcohol, in which the red matter is insoluble. This red substance appears to be a fatty ethereal salt of cholesterol, identical with the so-called carrotin. A. G. B.

The Fruit of Capsicum annum. By T. Pabst (*Arch. Pharm.*, **230**, 108—134).—The alkaloïd-like substance obtainable in traces from the fruit of *Capsicum annum* is not a normal constituent thereof, but a decomposition product which is formed during the storage of the fruit, or else by the action of chemical agents. The pungent substance, the so-called capsaicin, behaves towards metallic salts as an amorphous acid, and is intimately mixed with a red colouring matter; the latter resists all attempts to separate it from the acid, and it is an open question whether the colouring matter is combined with the acid or not. The pungent substance is also closely associated with free fatty acids, namely, oleïc, palmitic, and stearic acids. The colouring matter was not actually identified with carrotin, although it appears to be a fatty ethereal salt of cholesterol (compare Thresh, Abstr., 1878, 233). A. G. B.

Analytical Chemistry.

Estimation of Glycerol in Sweet Wines. By M. T. Lecco (*Ber.*, **25**, 2074—2075).—The author adds a large excess of calcium hydroxide to the wine, namely, 1 gram per 10 c.c. The estimation of the glycerol is then carried out as usual by the method previously described (*Chem. Zeit.*, **14**, 504). E. C. R.

Behaviour of Aldehydes and Ketones with Aromatic Nitro-compounds. By B. v. Bittó (*Annalen*, **269**, 377—382; compare this vol., p. 924).—Many aldehydes and ketones give with certain aromatic nitro-compounds in presence of potash, and of alcohol also if necessary for solution, a more or less intense colour reaction; in the case of metadinitrotoluene, for example, a blue, in the case of α-dinitronaphthalene, an intense red, coloration is produced.

The author gives in a table the results of an examination of the behaviour of a large number of aldehydes, ketones, and ketonic acids with metadinitrobenzene, in presence of alkali; the effect produced by the subsequent addition of an organic acid is also stated.

From his observations he draws the conclusion that a colour reaction is given by all fatty aldehydes and fatty ketones which contain a non-substituted $CH_n{\cdot}CHO$ or $CH_n{\cdot}CO$ group respectively, by all mixed ketones, and by those aromatic aldehydes which contain a fatty radicle. F. S. K.

Volumetric Estimation of Peptones in Urine. By Roux (*J. Pharm.* [5], **25**, 544—545).—Fehling's solution run into a dilute solution of peptone passes through a colour change, light-blue, blue-violet, lilac, and rose-purple, to a greyish tint. The peptone solution is freed from albumin and reducing compounds, and decinormal Fehling's solution is employed, the titration finishing with the rose-purple tint. 1 c.c. of solution equals 0·004 gram of peptone. After a little practice, very concordant results can be obtained. J. T.

Colorimetric Estimation of Hæmoglobin. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **16**, 505—513).—It is recommended that the standard of comparison in the colorimetric estimation of blood pigment should be a normal solution of carbonic oxide hæmoglobin instead of the tinted glass, carmine, &c., at present largely used. The carbonic oxide hæmoglobin for comparison should be prepared in large quantities, and in well-stoppered bottles it keeps for years. Its strength can be estimated in a sample. The liquid to be investigated should, by means of a stream of carbonic oxide, have its hæmoglobin converted into carbonic oxide hæmoglobin. It is then diluted until its colour is the same as that of the standard. The amount of dilution being known, the strength of the solution is easily ascertained. The instrument used is termed a capillary double pipette, and the principle of it can be understood by reference to the accompanying diagram representing a transverse section. It consists of three glass



plates with brass side walls (the darker shading in the figure); the two cavities are divided into four by two highly polished glass plates (shaded lighter in the figure). The remaining two compartments are filled respectively with the standard solution and the liquid to be investigated. The advantage claimed for the instrument is that, as optically a mere line separates the two liquids, the colour comparison is rendered extremely sharp. The instrument can also be used for spectroscopic and spectrophotometric observations.

W. D. H.

General and Physical Chemistry.

Influence of Boric Acid on the Electrical Conductivity of Dilute Alcoholic Solutions of Organic Acids. By G. Magnanini (*Gazzetta*, **22**, 541—558).—The author has arrived at the following conclusions respecting the effect produced by boric acid on the electrical conductivity of organic acids in solution:—(*a*) The addition of boric acid to the aqueous solution of organic acids containing no alcoholic hydroxyl never augments the electrical conductivity. (*b*) A greater or less increase in conductivity always attends the addition of boric acid to the aqueous solution of a hydroxy-acid which contains an alcoholic or phenolic hydroxyl in the α- or ortho-position relatively to the carboxyl group. (*c*) In the aqueous solution of a hydroxy-acid which does not contain the hydroxyl in the α-position to the carboxyl group, boric acid never causes an augmentation in the conductivity. These three laws give a method for solving the constitutions of a number of organic acids which are soluble in water; many such acids, however, are practically insoluble in water, and it becomes of importance to know whether a more or less dilute alcoholic solution of the acid obeys the above laws. This question the author has investigated, using aqueous solutions containing 18—73 per cent. of alcohol, and finds that the laws still hold.

The following acids were examined:—Trichlorolactic, β-hydroxybutyric, malic, levulinic, mucic, trichlorodiketopentamethylenehydroxycarboxylic, dibromoparahydroxybenzoic, ortho- and para-nitrosalicylic, ortho-, meta-, and para-cresotic, orthocoumaric, β-resorcylic, protocatechuic, guiacolcarboxylic, orsellinic, pyrogallolcarboxylic, gallic, α-hydroxynaphthoic, and quinic acids. In all these cases, the results obtained were consistent with the generally accepted constitutions of the acids.

The author has also studied the effect of boric acid on the conductivity of the sodium salts of certain organic acids, but with very little result up to the present. W. J. P.

Diffusion in Aqueous Solutions. By S. Arrhenius (*Zeit. physikal. Chem.*, **10**, 51—95).—By means of a modification of Scheffer's apparatus (*Zeit. physikal. Chem.*, **2**, 391), the author has investigated the rate of diffusion of a large number of substances, both electrolytes and non-electrolytes, in aqueous solution. The error in the diffusion constant he estimates in the most unfavourable circumstances to be 2 per cent., and, in general, the error of the single determinations to be about 1 per cent.

When a non-electrolyte (for example, alcohol) replaces a portion of the water of a salt solution, then the rate of diffusion into the mixed solvent is less than the rate when pure water alone is used. For not too great concentrations (of the non-electrolyte in water),

the following relation holds good between the coefficient of diffusion and the concentration :—

$$D_x = D_0 (1 - \frac{\alpha}{2} x)^2,$$

where D_0 is the diffusion coefficient in pure water, D_x that in an x-normal solution of the non-electrolyte, and α a constant depending on the nature of the non-electrolyte. This formula is similar to the formula which expresses the effect of an addition of a non-electrolyte on the electrical conductivity of an aqueous salt solution (compare this vol., p. 1038), the coefficient α being nearly the same in the two cases. α is not greatly dependent on the nature of the diffusing substance.

When an electrolyte is added to the solvent instead of a non-electrolyte, there is usually a diminution of the diffusion constant, the influence on the rate of diffusion being very similar to the influence on the fluidity, as the following table shows :—

		Diffusion.	Fluidity.
1-n	KCl	0·997	1·013
„	NH_4Cl	0·986	1·024
„	$NaNO_3$	0·97	0·937
„	NaCl	0·915	0·932
„	$\frac{1}{2}(Na_2SO_4)$	0·845	0·814
„	$CH_3 \cdot COONa$	0·75	0·719

The author discusses at length the mechanism of diffusion phenomena, and shows that whilst the osmotic pressure theory, as applied by Nernst, explains the observed facts, the assumption of an attractive force between the molecules of the solvent and the molecules of the dissolved substance fails to do so. He is of opinion, however, that the relation between osmotic pressure, π, and concentration, K, may best be expressed by the formula $\pi = AK + BK^2$, where B is a constant which expresses the difference of the attractions of the dissolved for the solvent molecules and of the dissolved molecules amongst themselves. In dilute solutions, the second term vanishes, as compared with the first, and the osmotic pressure is then proportional to the concentration.

When hydrochloric acid diffuses, not into pure water, but into a solution of one of its salts, say of sodium chloride, the diffusion constant, instead of diminishing, increases. The author shows that this apparently anomalous case is capable of easy explanation on the assumption of the theory of electrolytic dissociation, and, from this hypothesis, calculates the constants for a number of similar cases. A selection of his results is contained in the table on page 1267.

The constant of diffusion has long been known not to be quite independent of the concentration of the diffusing solution, sometimes increasing, sometimes diminishing, with this. The author shows, on the osmotic pressure theory, that the relation between them may be expressed (for a non-electrolyte) as follows :—

$$K_c = K_\infty (1 + DC)(1 - \alpha C/2)^2,$$

Diffusing substance.	Solvent.	Diffusion constant (at 12°). Found.	Calculated.
HCl (1·04-norm.) .	Water	2·09	—
,, ..	0·67-*n* NaCl ..	3·51	3·58
,, ..	0·1-*n* ,, ..	2·50	2·43
,, ..	0·75-*n* KCl ...	4·22	4·08
,, ..	0·25-*n* ,, ...	3·08	3·10
NaOH (0·54-norm.)	Water	1·15	—
,,	0·25-*n* NaCl ..	1·90	2·02
,,	0·067-*n* ,, ..	1·51	1·52
,,	1-*n* ,, ..	1·98	2·17
,,	3-*n* ,, ..	2·30	2·40

where K_c is the diffusion constant for the concentration C, K_∞ the constant for infinite dilution, and α and D two coefficients which may be determined. According as D is greater or less than α, the diffusion constant will increase or decrease with the concentration. Examples are given, and the case of electrolytes is also discussed, the author replying to objections raised by Wiedeburg (Abstr., 1891, 383) against the new theory, and criticising the experimental method adopted by him.

By thermodynamical reasoning, the author shows that the osmotic pressure is proportional to the lowering of the freezing point for depressions less than 2°. J. W.

Determination of the Specific Gravity of Gases. By H. Moissan and H. Gautier (*Compt. rend.*, **115**, 82—86).—A flask fitted with a stop-cock is filled with perfectly dry air and weighed. The greater part of the air is then pumped out, and a known volume (about 100 c.c.) of the gas under examination is transferred to the flask by means of a graduated gas pipette. Dry air is allowed to enter the flask until the pressure is only slightly below that of the atmosphere, and the flask is again weighed. The difference between the first and second weighings, after correction for pressure, is the difference between the weight of the measured volume of gas and an equal volume of air. The error does not exceed 1 per cent., even in the case of gases whose sp. gr. is almost the same as that of air.

C. H. B.

Passage of Substances in Solution through Mineral Filters and Capillary Tubes. By C. Chabrié (*Compt. rend.*, **115**, 57—60).—In a previous note (*Compt. rend.*, **113**, 600), the author has shown that when albuminous urine is filtered through porcelain, the urea passes more quickly than the albumin, and when defibrinated blood is treated in the same way, the albumin and hæmoglobin concentrate in the later portions of the filtrate, and the hæmoglobin filters more slowly than the albumin. When a solution of urea and uric acid is filtered, the two substances pass through with equal rapidity. The results show that when two substances of large but unequal molecular volumes are filtered, that with the smaller volume filters more

quickly than the other, whilst with two substances of small though unequal molecular volumes the difference is too small to be recognised.

When a solution of albumin is passed through a capillary tube, of 0·05 mm. mean diameter, the albumin passes through less rapidly than the water. There is consequently a concentration of albumin in the reservoir, and if the solution becomes too strong, its passage through the tube ceases. No chemical change takes place, for if the whole of the liquid is forced through the tube, its composition at the end of the experiment is the same as at the beginning.

A solution of urea and Congo-red (mol. wt. 826) showed no difference in the rates of transpiration of its constituents. It follows that the phenomenon is only shown by substances with molecular weights which, like that of albumin, approach 10,000 to 15,000.

C. H. B.

Dissociation Constants of Stereoisomeric Nitrogen Compounds. By A. Hantzsch and A. Miolati (*Zeit. physikal. Chem.*, **10**, 1—33).—α-Oximido-acids which (according to the hypothesis advanced by Hantzsch and Werner to explain the stereoisomerism of the nitrogen compounds) have the carboxyl and the hydroxyl groups in the neighbouring positions are considerably feebler than the corresponding acids with these groups in the opposed positions. Thus phenylsynketoximecarboxylic acid, $\begin{matrix}C_6H_5\cdot C\cdot COOH\\ \|\\ N\cdot OH\end{matrix}$, has a dissociation constant of 0·18, whilst phenylantiketoximecarboxylic acid, $\begin{matrix}C_6H_5\cdot C\cdot COOH\\ \|\\ HO\cdot N\end{matrix}$, has a constant of 1·55. Both acids are feebler than the ketonic acid (phenylglyoxylic acid, $K = 6{\cdot}31$) from which they are derived. The anti-acid in aqueous solution passes gradually into the syn-acid. The progress of this reaction may be followed by determining the electrical conductivity at different times. In the case of β-oximido-acids, the anti-compound is weaker than the syn-compound.

The authors obtained the following numbers for dioximido-acids :—

Glyoximecarboxylic Acids.

$\begin{matrix}H\cdot C\\ \|\\ HO\cdot N\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ HO\cdot N\end{matrix}$, $K = 0{\cdot}417$; $\begin{matrix}H\cdot C\\ \|\\ HO\cdot N\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ N\cdot OH\end{matrix}$, $K = 0{\cdot}285$.

Methylglyoximecarboxylic Acids.

$\begin{matrix}CH_3\cdot C\\ \|\\ N\cdot OH\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ HO\cdot N\end{matrix}$, $K = 1{\cdot}39$; $\begin{matrix}CH_3\cdot C\\ \|\\ N\cdot OH\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ N\cdot OH\end{matrix}$, $K < 1{\cdot}39$.

Glyoximedicarboxylic Acids.

$\begin{matrix}COOH\cdot C\\ \|\\ N\cdot OH\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ HO\cdot N\end{matrix}$ $K = 6{\cdot}22$; $\begin{matrix}COOH\cdot C\\ \|\\ NO\cdot N\end{matrix}\!\!-\!\!\begin{matrix}C\cdot COOH\\ \|\\ N\cdot OH\end{matrix}$, $K = 1{\cdot}05$.

The acids with the smaller constants are the more stable, the

stronger acids being gradually converted into them, by autocatalysis, in aqueous solution. J. W.

Affinity Coefficients of Acids. By E. Lellmann (*Annalen*, **270**, 204—208; compare Abstr., 1891, 638 and 1149).—The author and Schliemann have measured the relative affinity of a number of acids by a spectro-photometric method, analogous to that previously employed by the author and Gross in the case of bases, and described in the following abstract. The results obtained, within very wide limits of concentration, are in complete agreement with Guldberg and Waage's law, but they cannot be compared or brought into line with Ostwald's values of the electrical conductivity of the acids; the author considers that the affinity constants determined by the spectro-photometric method express in a more simple and direct way than can be done by the dissociation constants, the connection which exists between chemical change and the nature of the interacting substances. F. S. K.

Affinity Coefficients of Acids. By E. Lellmann and J. Schliemann (*Annalen*, **270**, 208—235).—The method employed for the measurement of the relative affinity of acids is, briefly, the following:—A measured quantity (25 c.c.) of a solution of 2 milligram equivalents (0·448 gram) of pure metahydroxyanthraquinone in 1 litre of 96 per cent. alcohol is mixed with a definite quantity of a solution of known strength of the pure barium salt of the acid, the mixture diluted to 50 c.c., and examined with a spectro-photometer; its absorption is then compared with that of a solution of the same quantity of metahydroxyanthraquinone in excess of barium hydroxide. The alcohol and the water used in the preparation of the solutions are carefully purified from basic substances by distillation over potassium hydrogen sulphate, and the glass vessels in which the solutions are kept are carefully freed from alkali by prolonged digestion with very dilute sulphuric acid; in cases where the barium salt is too sparingly soluble, a solution of the potassium salt is employed.

The results of the measurements are given in the following table: κ denotes the number of equivalents of the salt of the acid, compared with the number of equivalents of hydroxyanthraquinone salt, which are present in a solution containing equivalent quantities of hydroxyanthraquinone acid and base.

	κ.		κ.
Formic acid	61·97	Paramidobenzoic acid	7·60
Acetic acid	14·33	Nicotinic acid	43·02
Cinnamic acid	17·74	Picolinic acid	18·75
Benzoic acid	20·71	Isonicotinic acid	47·36
Orthotoluic acid	21·91	Lactic acid	39·94
Metatoluic acid	16·47	α-Hydroxyisobutyric acid	37·94
Paratoluic acid	15·22	Propionic acid	11·68
Orthamidobenzoic acid	11·40	Cinchonic acid	61·61
Metamidobenzoic acid	15·56		

The authors give a table comparing the affinity constants measured in this way with those determined by Ostwald; they are of opinion that the lack of agreement between the two series of observations is due to the fact that different solvents were used in the two cases. Special experiments proved clearly that the nature of the solvent has, under certain circumstances, a very considerable influence on the affinity constants as determined either by the spectrophotometric or by the electrical method, but even when the same solvent is employed in both cases the results do not agree.

F. S. K.

Autocatalysis. By U. Collan (*Zeit. physikal. Chem.*, **10**, 130—140).—The author has investigated the reaction velocity of the transformation of hydroxymethylbenzoic acid into phthalide in aqueous solution, and finds that it obeys the formula $-\frac{dC}{dt} = \delta C(1 - \delta)C \cdot K$, where C is the concentration, δ the proportion of the acid dissociated, and K the constant of the reaction. This is in agreement with the results obtained by Henry (p. 1303). Equations are also developed for the catalysis proceeding in presence of an acid (glycollic acid) which has the same dissociation constant as the acid catalysed. The agreement between calculation and experiment is good.

J. W.

Correlation of Oxygen and Hydrogen Compounds of the Elements. By F. Flavitzky (*J. pr. Chem.* [2], **46**, 57—85).—The compounds of non-metallic elements with hydrogen and oxygen can be referred to types consisting of hydroxyl, or of hydroxyl and hydrogen, combined with the element. The number of hydroxyl groups and hydrogen atoms is determined by the group of the periodic system into which the element falls. Thus, the stable hydroxy-compounds of an element in the fifth group can be regarded as anhydrides, derived by the loss of water from an original type consisting of 5 hydroxyl groups, or m hydroxyl groups and $5-m$ hydrogen atoms, united with the element. The tendency of the hydroxy-halogen acids to form stable hydrates, the inactivity of anhydrous hydrogen chloride, and the existence of many hydrated and double salts are explicable according to the author's theory, and many examples are adduced in the paper.

A. G. B.

Inorganic Chemistry.

Mutual Displacement of Haloïds. By Miss P. Lazareff (*J. Russ. Chem. Soc.*, **22**, 383—385).—The chlorides of sodium and potassium were sealed up in tubes, along with bromine and with iodine, dissolved in carbon tetrachloride, and were allowed to remain for eight months at the ordinary temperature in the absence of light.

Similar experiments were made with iodine and the bromides of sodium and potassium. No change took place. J. W.

Composition of Water, and Gay Lussac's Law of Volumes. By A. Leduc (*Compt. rend.*, **115**, 41—44).—The author has redetermined the gravimetric composition of water, using a modification of Dumas' method. The copper oxide was prepared by oxidising very thin sheets of electrolytic copper, and was afterwards reduced at the lowest possible temperature in pure and dry hydrogen, the tube being wrapped in platinum foil. The last two tubes of the condensing apparatus were surrounded by ice and salt. The results show that the atomic weight of oxygen is 15·88, whilst its sp. gr. with reference to hydrogen, according to the author's determination (Abstr., 1891, 1416), is 15·90. It follows that the atomic weights, as determined by Stas, should be multiplied by 0·995. The results afford remarkable confirmation of Gay Lussac's law of volumes, but show that this law, like that of Boyle, is only true within certain limits. C. H. B.

Efflorescence of Metallic Sulphates. By H. Baubigny and E. Péchard (*Compt. rend.*, **115**, 171—174).—The rate at which various sulphates lose their water of crystallisation when exposed to dry air is considerably increased when they are crystallised from slightly acid solutions. 8·0 grams of copper sulphate, for instance, crystallised by vacuum evaporation of a solution containing 0·15 per cent. of free sulphuric acid, lost 4·875 grams in 65 hours, whilst 7·3 grams, crystallised in the same way from a solution neutral to methyl-orange, lost only 0·013 gram under identical treatment. The hexhydrate of cobalt nitrate also is much less stable when crystallised from acid solutions, although the heptahydrate does not show this difference. Zinc sulphate, again, loses its water more rapidly when crystallised from acid solutions, although the amount actually lost is the same in either case, a dihydrate being left. The double sulphates of cobalt and potassium, and of zinc and potassium, and the double ammonium alum of aluminium and chromium, behave in the same way, although the acidity of the mother liquor has to be much more strongly marked before the effect is apparent. Jn. W.

Action of Nitric Oxide on Metallic Oxides. By P. Sabatier and J. B. Senderens (*Compt. rend.*, **114**, 1476—1479).—The experiments described in a previous paper (this vol., p. 1151) have shown that nitric oxide acts as an oxidising agent on many metals and metallic oxides. Nitric oxide, however, tends to combine with oxygen to form nitric peroxide, and hence under some conditions acts as a reducing agent. At 150°, the reaction $NO + O = NO_2$ develops +16·7 Cal. The heats of formation of mercuric, cupric, ferric, and stannic oxides, by combination of the lower oxides with an atom of oxygen, are respectively +20, +38·2, +51·2, and +66 Cal., and are consequently higher than the heat of formation of nitric peroxide from nitric oxide. Direct experiment shows that these oxides are not reduced by nitric oxide below 500°. There is likewise no reduc-

tion in the analogous cases of molybdic, tungstic, titanic, and vanadic anhydrides, and uranic oxide.

On the other hand, the combination of silver, chromic oxide, and lead monoxide with one atom of oxygen to form respectively silver monoxide, chromic anhydride, and lead dioxide develops in the first case +7 Cal., in the second +2·1 Cal., and in the third +12·2 Cal. only. Chromic anhydride is reduced by nitric oxide at the ordinary temperature; silver oxide is reduced at 170°, and lead dioxide at 315°. Manganese dioxide is reduced to the sesquioxide by the action of nitric oxide at 400°.

When nitric oxide is passed into water containing lead dioxide, silver oxide, or manganese dioxide, appreciable quantities of nitrite are formed, even when air is entirely absent. The reaction is most distinct in the case of the lead compound, a solution containing 4 grams of lead nitrite per litre can be obtained; if the passage of the gas is prolonged, or if the liquid is concentrated, basic lead nitrite is formed. C. H. B.

Decomposition of Basic Nitrates by Water. By G. Rousseau and G. Tite (*Compt. rend.*, **115**, 174—175).—Copper subnitrate is completely decomposed by water at 150—160° into copper oxide and nitric acid, probably because the heat of dissolution of nitric acid in water, which is known to rise with the temperature, eventually becomes greater than its heat of combination with the oxide. The phenomenon appears to be fairly general, and occurs, for instance, with zinc, cadmium, and calcium subnitrates. Bismuth subnitrate may be completely decomposed into the oxide and acid by prolonged treatment (90 hours) with water at 200—205°. The water must be frequently changed, and marble must be added to take up the acid. Uranium subnitrate, prepared by heating the crystallised nitrate with marble in sealed tubes at 180—200°, and crystallising the product from alcohol, contains less acid the longer it is treated. Water completes the decomposition, the hydrate U_2O_3,H_2O being left. Jn. W.

Phosphorus Bromonitride. By A. Besson (*Compt. rend.*, **114**, 1479—1481).—When the compound of ammonia and phosphorus pentabromide (Abstr., 1891, 398) is heated at 200° under reduced pressure, it yields a small quantity of a white, crystalline sublimate insoluble in water. The yield can be increased by operating in the following manner:—The product of the action of dry ammonia on phosphorus pentabromide is heated in sealed tubes at 250—275° with about twice its weight of phosphorus pentabromide for 12 hours, and the semi-fluid magma obtained is heated under reduced pressure. Unaltered phosphorus pentabromide first sublimes, and at 200° the white sublimate forms and can be purified by resublimation in a vacuum. The product thus obtained is *phosphorus bromonitride*, PBr_2N. It forms colourless, highly refractive, seemingly rhombohedral crystals, which melt at 188—190° and begin to sublime at 150° in a vacuum; they are soluble in ether, less soluble in carbon bisulphide or chloroform, and insoluble in water.

A larger yield of the chloronitride (this vol., p. 1152) is obtained if

a layer of phosphorus pentachloride is first formed on the walls of a large flask by the action of chlorine on the trichloride, and then treated with ammonia until superficially saturated. The solid crust is then broken up and heated under reduced pressure. It will be seen that under these conditions the ammoniacal phosphorus pentachloride is heated in presence of the unaltered pentachloride which formed the lower part of the crust on the walls of the flask.

C. H. B.

Silicon Tetrachloride. By G. Rauter (*Annalen*, **270**, 235—266).—When silicon tetrachloride is heated at 270—370° severally with beryllium, magnesium, zinc, and aluminium, it is partially decomposed, but no reaction occurs with sulphur or with iron; it is not acted on by carbon bisulphide or chloride of sulphur, or by the sulphides of sodium, potassium, mercury, arsenic, and antimony even at 350—400°, but it is decomposed to a very slight extent by potassium bromide and by potassium iodide with liberation of silicon and a halogen.

Silicon tetrachloride is decomposed by nearly all metallic oxides, either at the ordinary temperature or on heating, with formation of silica; also by alkali carbonates and by nitrite, nitrate, chromate, dichromate, sulphate, permanganate, and chlorate of potassium; it is not decomposed by the oxides of carbon.

When silicon tetrachloride is heated with butyric acid at 150—160°, silica, hydrogen chloride, and butyric chloride are formed; with acetic anhydride, it yields acetic chloride and silica, but with phthalic anhydride there seems to be no action. Lead formate and silicon tetrachloride react at 240—250°, yielding silica, lead chloride, carbon monoxide, and hydrogen chloride; potassium acetate and silicon tetrachloride give potassium chloride, silica, and acetic chloride. Ethyl butyrate and ether are not acted on by silicon tetrachloride at 150—160°.

F. S. K.

Examination of Different Forms of Carbon. By J. Wiesner (*Monatsh.*, **13**, 371—410).—The author has subjected the various forms of carbon to the action of a mixture of sulphuric acid and potassium dichromate, and observed under the microscope the changes which take place. The chief results are as follows:—

The purest form of charcoal, obtained by heating the soot from a gas flame successively in currents of chlorine, nitrogen, and hydrogen, is slowly attacked by chromic mixture in the cold, and more quickly on warming; the action is much more rapid than with any of the other varieties of carbon, probably owing to its very finely divided state. Lignite is seen under the microscope to consist of brown, transparent particles, which rapidly become colourless on treatment with chromic mixture, leaving a skeleton tissue of cellulose, the histological character of which is frequently no longer recognisable. If the action of the chromic mixture is continued, this is also destroyed.

All the other varieties examined, namely, anthracite, bituminous coal, wood charcoal, soot, and graphite, contain a small quantity of an easily oxidisable substance, which is quickly dissolved by the chromic mixture, leaving a residue which is only very slowly attacked by it, no visible change taking place for weeks at the ordinary tempera-

ture. Anthracite consists almost entirely of amorphous carbon with a small quantity of a deep brown substance, which is slowly attacked by the oxidising agent, but leaves no residue of cellulose. Bituminous coal behaves in this, as in other respects, like a mixture of lignite and anthracite, and therefore leaves small quantities of cellulose on treatment with the acid mixture. Wood charcoal prepared at a low temperature, such as is used in the manufacture of gunpowder, is completely dissolved by chromic mixture, leaving at a certain stage a skeleton of cellulose which dissolves after a time. The wood charcoal obtained at a high temperature is, on the other hand, only attacked to a slight extent. Freshly prepared soot consists partly of fine black particles, which are hardly attacked by the acid, and partly of oily drops; the soot deposited from the atmosphere contains similar particles of carbon, which are sometimes united to form dendritic or irregular aggregates. Finely divided graphite also contains very small quantities of an oxidisable substance, and, although less acted on by chromic mixture than the amorphous variety, is not totally indifferent to the reagent.

The black lung pigment, which collects in the human lungs during life, behaves under the microscope in exactly the same manner as the black soot particles, and remains unaltered after several weeks' treatment with chromic acid. The melanin pigments, on the other hand, are rapidly attacked by the acid, the action being frequently complete in a few minutes. The pigment must therefore be derived from the soot contained in the air, and is not, as has been frequently supposed, formed within the organism itself.

The author also corrects the statement that has been made as to the transparency of amorphous carbon in a finely divided condition, his own observations having led him to the contrary conclusion.

H. G. C.

Supersaturated Aqueous Solutions of Carbonic Anhydride. By L. Pratesi (*Gazzetta*, **22**, 493—498).—The author has observed that certain mineral springs contain a larger quantity of carbonic anhydride in solution than is indicated by Bunsen's observations. For example, a mineral water from Contursi, in Salermo, issues at a temperature of 40° and contains 1·7605 grams of free carbonic anhydride per litre. Ordinary seltzer water, when drawn from the siphon and allowed to remain in the air for half an hour, still contains 1·901 litres of carbonic anhydride at 8° and 764·75 mm. pressure per litre: under these conditions of temperature and pressure, Bunsen found that distilled water dissolves 1·289 litres only of the gas. Distilled water, when saturated with carbonic anhydride in a siphon under pressure and then drawn off and allowed to remain for half an hour, was found to contain 1·858 litres of the gas at 9·5° and 770·65 mm. pressure per litre. The quantity of carbonic anhydride dissolved by 1 litre of distilled water at this temperature and pressure is 1·225 litres according to Bunsen.

It would hence seem that water first saturated with carbonic anhydride under pressure and then left for a short time under the ordinary pressure, contains a much larger quantity of carbonic anhydr-

ide than water simply saturated with the gas under ordinary pressure. W. J. P.

Lithium Bromate. By A. Potilitzin (*J. Russ. Chem. Soc.*, **22**, 392—393).—Lithium bromate was prepared in solution by the action of lithium sulphate on barium bromate. The solution was evaporated on the water-bath to incipient crystallisation, and afterwards placed over sulphuric acid in a bell jar. Anhydrous lithium bromate, $LiBrO_3$, crystallised out in apparently rhombic crystals, with well developed pyramidal faces. The hydrated salt, $LiBrO_3,H_2O$, was also obtained. J. W.

Double Chlorides of Lithium and Metals of the Magnesium Series. By A. Chassevant (*Compt. rend.*, **115**, 113—115).—Manganese, iron, nickel, and cobalt form isomorphous, double chlorides with lithium of the type $MCl_2,LiCl,3H_2O$. They have the colour of the anhydrous chloride of the dyad metal that they contain, and are easily dissociated by water, but are stable in presence of excess of lithium chloride. They form acicular crystals which, in a dry atmosphere, effloresce and lose hydrogen chloride. C. H. B.

Rate of Decomposition of Calcium Chlorate by Heat. By A. Potilitzin (*J. Russ. Chem. Soc.*, **22**, 333—346; compare Abstr., 1890, 696).—Calcium chlorate was prepared in the pure state by crystallisation of the commercial salt from aqueous solution. It crystallises with 2 mols. H_2O, and deliquesces in the air. The author could not confirm Wächter's observation that the salt melts on rapid heating to a temperature above 100°, but found that it is decomposed into the anhydrous salt and water. The anhydrous salt may be obtained crystalline by allowing the partially fused mass to evaporate slowly over sulphuric acid. The hydrated salt loses all its water of crystallisation on prolonged heating at 100°.

Anhydrous calcium chlorate begins to give off oxygen before it fuses, but between the limits 300—350° it melts after having lost from 3 to 5 per cent. of its weight of oxygen. The rate of decomposition at 330° increases until about 60 per cent. of the total oxygen has been evolved, after which it continually diminishes, the fused mass becoming solid when the salt has lost about 80 per cent. of its oxygen. The calcium chloride remaining is in the form of thin, transparent, needle-shaped crystals. On being dissolved in water, the residue exhibits an alkaline reaction. In the accompanying table (p. 1276), the connection between the composition of the mass and the quantity of oxygen given off is indicated. The temperature of experiment was 329—330°, and the numbers express percentages.

For various stages of the reaction at different temperatures, the author gives equations similar to those expressing the decomposition of strontium chlorate (Abstr., 1890, 697). The quantity of perchlorate formed is relatively much less than in the case of the strontium and barium salts.

Oxygen evolved (loss of weight).	Total chlorate decomposed.	Chlorate converted into chloride.	Chlorate converted into perchlorate.
6·00	13·48	13·20	0·28
9·40	21·59	20·40	1·17
10·78	25·13	23·77	1·36
15·00	34·47	32·51	1·87
20·97	47·78	45·51	2·26
27·43	61·56	59·21	2·34
31·77	70·32	68·01	2·31
39·74	86·12	84·23	1·92

J. W.

Basic Calcium Nitrate. By A. Werner (*Compt. rend.*, **115**, 169—171).—Milk of lime is added to a cold, saturated solution of calcium nitrate until it ceases to be dissolved; the solution is then shaken, and after some minutes sets to a semi-solid mass of long needles. This is protected from carbonic anhydride, and left for two or three days, after which it is collected on an asbestos filter by means of a filter pump. The *basic nitrate* thus obtained is dried on glazed porcelain in an atmosphere free from carbonic anhydride. It has the composition $Ca(NO_3)_2,Ca(OH)_2,2\frac{1}{2}—3H_2O$, and loses its water of crystallisation at 160°. It is decomposed by water into calcium nitrate and hydroxide. The heat of formation of the anhydrous salt is +2·0 Cal., and a further amount of 8·4 Cal. is developed in the formation of the hydrated salt. Jn. W.

Influence of the Composition of the Glass of Slides and Cover-glasses on the Durability of Microscopic Objects. By R. Weber (*Ber.*, **25**, 2374—2377).—It has been observed that objects well sealed between the cover-glass and slide sometimes lose the sharpness of their outline after a short time, and the glass becomes dim. The author finds that this is due to the composition of the glass. Those glasses which contain an excessive amount of alkali soon lose their lustre and become dim when exposed to moisture. The analysis of a colourless object glass, which did not retain its lustre, gave numbers corresponding with the ratio

$$SiO_2 : CaO : K_2O,Na_2O = 8·2 : 1 : 1·74.$$

Slightly green glasses, which contain more lime and less alkali, are more stable on exposure to air. Analyses of two sorts of cover-glasses, of which the first retained its lustre and the second did not, gave the ratios $SiO_2 : CaO : (K_2O,Na_2O) = 4·7 : 1 : 0·9$ and $6·6 : 1 : 1·1$ respectively. E. C. R.

Action of Potassium Sulphate on Strontium Carbonate. By E. Kouklin (*J. Russ. Chem. Soc.*, **22**, 322—326).—Strontium carbonate (1 mol.) was boiled up with a solution of potassium sulphate (40 mols.). After the boiling was over, the liquid was filtered and the precipitate washed with hot water. The mixed precipitate was treated with hydrochloric acid, and, to the solution obtained, alcohol was added to precipitate any strontium sulphate remaining

dissolved; this was added to what remained of the original precipitate; the whole was then washed with 80 per cent. alcohol and weighed. The strontium in the filtrate was precipitated by sulphuric acid, and weighed as sulphate.

The following numbers were found, corrections having been made for the solubility of the sulphate in water:—

Experiment.	Duration of boiling.	Strontium carbonate changed into sulphate.
I	5 hours	43·27 per cent.
II	17 „	56·74 „
III	48 „	65·88 „
IV	90 „	70·27 „

The number in Experiment IV is probably the limiting number, or very near it. There would thus be in the solution, which is in equilibrium with mixtures in any proportions of strontium sulphate and strontium carbonate, 55 mols. of potassium sulphate to 1 mol. of potassium carbonate.

0·9077 gram of strontium sulphate, boiled with a solution containing a large excess of potassium sulphate and carbonate in the proportion of 5 parts of the former to 1 of the latter, was all converted into carbonate, except 0·011 gram. But the quantity of sulphate which would go into solution in the liquid employed for boiling and for washing was 0·048 gram. All the strontium sulphate left unchanged was thus dissolved. Consequently Rose's method for separating barium from strontium and calcium, by boiling the solution of their salts with a solution containing potassium carbonate and sulphate, may be employed if this solution contains 1 part of the carbonate to 5 of the sulphate, for then any sulphate of strontium formed will pass into solution, and thus be separated from the barium sulphate produced at the same time. J. W.

Preparation of Pure Strontium Salts. By Barthe and Falières (*Bull. Soc. Chim.* [3], **7**, 104—108).—The authors have examined the various processes recommended for the preparation of pure strontium salts, and find that none of those previously described gives products free from barium or calcium. The process of precipitating the barium as chromate, boiling, filtering, and precipitating the filtrate with sodium carbonate gives a product which contains barium, as does also the carbonate obtained by the prolonged action of ammonium carbonate solution (10 per cent.) on impure precipitated strontium sulphate; the latter process is, however, the best of those examined. Barium was also detected in the product got by boiling impure precipitated strontium sulphate with a solution of potassium sulphate and carbonate. The addition of small quantities of alkaline sulphates to the hot or cold solutions of a strontium salt contaminated by barium gives the worst results of all the methods ordinarily employed; better results are obtained by fractional precipitation with dilute sulphuric acid (0·2 per cent.).

The authors give the following process for obtaining a pure

strontium salt from a barytostrontianite containing iron, aluminium, magnesium, calcium, and barium as impurities. The mineral, or the sulphide resulting from the reduction of the sulphate, is dissolved in such a quantity of hydrochloric acid (20 per cent.) as to leave a little undissolved. The aluminium and iron are precipitated by ammonia, filtered off, and excess of sulphuric acid added. The precipitate is washed first with dilute sulphuric acid (1—2 per cent.), and finally with water; it is thus freed from magnesium and calcium. It is now digested in the cold for some days with ammonium or potassium carbonate solution (10 per cent.), washed well, the residue treated with dilute hydrochloric acid, and the solution decanted; after remaining for 24 hours, this is filtered, and 200 grams of hydrochloric acid (sp. gr. 1·17) per litre are added to it, together with 2 or 3 grams of precipitated strontium sulphate, which may contain barium. After some hours, the solution is filtered, evaporated to dryness, dissolved in water, filtered, and crystallised. The spectrum given by the salt thus obtained shows strontium to be the only metal present. W. J. P.

Action of Hydrogen Peroxide on the Hydrated Oxides of Cadmium, Zinc, and Magnesium. By V. Kouriloff (*J. Russ. Chem. Soc.*, **22**, 171—194).—The author has made a careful investigation of this reaction, which has been studied by Thénard and others, but not hitherto elucidated. On heating the hydrated oxides of cadmium and zinc with a solution of hydrogen peroxide, basic peroxides have been obtained, which, on analysis, were found to have the formula $MO_2,M(OH)_2$. The above metals differ, therefore, in this point from the metals of the calcium group, which, under similar conditions, give products of the formula MO_2. The capacity of the metals for uniting with oxygen, as exemplified by the zinc and cadmium compounds, increases with the atomic weight, just as it does with the metals of the calcium group. The compounds obtained are very stable. They may be looked on as salts, in which the peroxides act as anhydrides like CO_2, SiO_2, &c., the hydrated monoxides as basic oxides. Thus these hitherto unisolated peroxides occupy an intermediate position between the acid peroxides CO_2, SiO_2, &c., and the neutral peroxides, SrO_2, BaO_2, &c.; and, like the peroxides MnO_3 and Mn_2O_7, although they do not exist in the free state, they yield stable compounds with other oxides. These compounds may also be regarded as hydrates of the formula $M(OH)_4$ of an oxide MO_3, in which a bivalent metal has taken the place of 2 atoms of hydrogen. These products are formed by direct addition of the oxygen of the hydrogen peroxide to the hydrated oxides of cadmium and zinc. The experiments on the magnesium compounds are incomplete. M. F.

Action of Nitric Acid on Metals. By C. Montemartini (*Gazzetta*, **22**, i, 250—265).—In the experiments described in this paper, the metals cadmium, iron, nickel, and cobalt were respectively dissolved in nitric acid of various degrees of concentration, at least 20 times the amount of acid required for solution being used so as to exclude secondary reactions as far as possible.

The experiments were principally carried out at a temperature of 8°, and the results are given in a series of tables. From these it appears that the evolution of ammonia is not limited to dilute solutions of nitric acid; thus, for instance, 0·00139 gram of ammonia was formed per gram of cadmium dissolved in 47 per cent. nitric acid; 0·0051 gram of ammonia per gram of iron dissolved in 52 per cent. nitric acid; and 0·01839 gram of ammonia per gram of cobalt dissolved in 42·8 per cent. nitric acid.

The gases evolved by the dissolution of 1 gram of the following metals in excess of 27·5 per cent. nitric acid were as follows:—

	NH_3.	HNO_2.	N_2O.	N.	NO.	Total grams.
Cadmium .	0·00197	0·00695	0·00570	0·00033	0·00216	0·01691
Iron	0·02493	0·00195	0·00422	0·00045	—	0·03553
Nickel	0·01874	0·00060	0·00749	0·00071	—	0·02754
Cobalt	0·02538	0·00077	0·00927	0·00467	—	0·04009

These numbers agree neither with the hypothesis that the dissolution of the metal is accompanied by the formation of nascent hydrogen, nor with that of the direct oxidation of the metal by the acid. No hydroxylamine is found amongst the final products of the reaction; this compound, if formed, must therefore be immediately destroyed by a secondary reaction. The nitric oxide is always of secondary origin, being derived in the case of cadmium, nickel, and cobalt from the decomposition of nitrous acid, and in the case of iron partly from the same source and partly from the oxidation of the ferrous salts first formed. In conclusion, the author holds that nitric acid acts as an oxidising agent in conjunction with the water present, the latter entering into the reaction. S. B. A. A.

Action of Nitric Acid on Zinc. By C. Montemartini (*Gazzetta*, **22**, i, 277—343).—The author has extended his investigations on the action of metals on nitric acid (preceding abstract) to zinc. The products formed in the reaction at a low temperature when the acid is in large excess are nitrous acid, hyponitrous acid, nitric oxide, nitric peroxide, nitrous oxide, nitrogen, and ammonia. Under the conditions mentioned, hydroxylamine is not found among the final products of the reaction, and free hydrogen is never evolved. With the exception of nitrous acid and nitric peroxide, the above products are formed, whatever the degree of concentration of the acid; no nitrous acid is, however, formed if the solution contains more than 30 per cent. of nitric acid, and no nitric peroxide if it contains less.

Ammonia.—At a temperature of 3—8°, the quantity in solution rises rapidly until the concentration of the acid is 10 per cent., then slowly until a maximum is attained between 40 and 45 per cent.; it falls abruptly at 47 per cent., and at 53 per cent. only a very small quantity is produced, which gradually diminishes with increased concentration, and may be represented by a straight line passing

through the zero point at 100 per cent. At a temperature of 85°, the maximum occurs at a concentration of 9 per cent., when it is equal to the production at the lower temperature; it then falls rapidly as the concentration is increased to 15 per cent.; beyond this point it may be represented by a line passing through the zero point when the concentration is 100 per cent.

Nitrous Acid.—At a temperature of 18—21°, the production increases rapidly with the temperature until a concentration of 14 per cent. of nitric acid is attained; it then falls with equal rapidity with increase of concentration to 30 per cent., at which stage nitrous acid ceases to appear among the final products.

Nitric Peroxide.—Between 18° and 22°, nitric peroxide is first formed at a concentration of 27 per cent. of acid; it increases slowly at first, rapidly between 64 per cent. and 72 per cent.; beyond 80 per cent. it remains almost constant.

Nitrous Oxide.—The formation of this compound takes place in comparatively large quantities and with great regularity. It reaches a maximum at a concentration of 40 per cent. acid and a minimum at 80 per cent.

Nitrogen is only formed in very small quantities in acid of all degrees of concentration.

The *velocity* of the dissolution of the zinc in nitric acid increases regularly with the concentration of the acid below 25 per cent.; it then falls slightly, remains constant between 33 per cent. and 42 per cent., then diminishes regularly, attaining its minimum value at a concentration of 68 per cent.; a considerable rise then takes place with increased concentration, but the previous maximum value is not again attained.

In conclusion, the author points out that the hypotheses that the reduction of nitric acid is effected by the direct action of zinc or by nascent hydrogen, both fail in certain cases, as a larger quantity of reduction products is formed than would be theoretically possible, and suggests that the water present enters into the reaction.

S. B. A. A.

The author in referring to previous researches makes no mention of those of Veley on the action of nitric acid on metals.—[Editors.]

A New Oxyiodide of Lead. By M. Gröger (*Monatsh.*, **13**, 510—515).—If a solution of 10 grams of iodine in 100 c.c. of absolute alcohol is mixed with one of 50 grams of crystallised lead acetate in 150 c.c. of water and 300 c.c. of absolute alcohol in a well-stoppered flask, allowed to remain at the ordinary temperature for 14—16 hours, and then filtered and mixed with 1 litre of distilled water, a brownish-red precipitate is formed, which has the composition PbO,PbI_2,I_3. The dry substance, which is brownish violet-red, is stable in dry air at the ordinary temperature, but when heated for a long time at 100°, or for a short time at 200°, loses iodine, and is converted into the basic lead iodide, PbO,PbI_2, of a chrome-yellow colour. When the original compound is treated with cold alcohol, the excess of iodine is not dissolved out, so that it must exist chemically combined; it is, however, dissolved out by a solution of potassium

iodide. Other reagents bring about a partial decomposition of the compound. C. F. B.

Specific Heat and Latent Heat of Fusion of Aluminium. By J. Pionchon (*Compt. rend.*, **115**, 162—165).—The experiments were made with commercial metal from Froges (Isère), containing 99·1 per cent. of aluminium, the rest being iron and silicon.

The amount of heat, q_t Cal., required to raise 1 gram of the metal from 0° to $t°$ is represented up to 580° by the equation—

$$q_t = 0{\cdot}393t - \frac{291{\cdot}86t}{1517{\cdot}8 + t},$$

and from 630° to 800° by the equation—

$$q_t = 0{\cdot}308t - 46{\cdot}9.$$

The specific heat thus rises slowly, but with increasing rapidity, from 0·201 at 0° to 0·2894 at 550°; the specific heat of the molten metal at 650° is 0·308.

From the above data, the latent heat of fusion is 80 Cal. The value calculated from the modulus of elasticity $\left(7287\frac{kg}{mm^2}\right)$, by comparison with silver according to Person's formula, is 38·38 Cal.

Between 580° and the melting point, 625°, the metal assumes a granular structure, and becomes very friable, falling to powder on the slightest pressure. Jn. W.

Aluminium. By Balland (*Compt. rend.*, **114**, 1536—1538).—The author finds that air, water, wine, beer, cider, coffee, milk, oil, butter, fat, urine, saliva, earth, &c., have less action on aluminium than on copper, lead, zinc, or tin. It is attacked by vinegar and by salt, but not to an extent sufficient to interfere with its use for the construction of domestic utensils. The author's results are in direct contradiction with the statements of Lubbert and Roscher, and agree with the experiments of Lunge and Schmid. C. H. B.

Utilisation of Burnt Pyrites in the Manufacture of Iron Salts. By A. Buisine and P. Buisine (*Compt. rend.*, **115**, 51—53).—Burnt pyrites has hitherto been little used for the preparation of iron salts because of an erroneous belief that the action of acids is slow and incomplete. Burnt pyrites ground to a fine powder is slowly attacked in the cold by sulphuric acid of 50° to 66° B., but when mixed with the calculated quantity of acid and heated at a temperature not exceeding 300°, solution is rapid and complete. The composition of the product at various temperatures, when heating is continued until there is no further loss of weight, is given in the following table (p. 1282). If the temperature exceeds 300°, the proportion of basic salt in the product gradually increases.

Ferric sulphate can replace ferrous sulphate in many of its industrial applications, and is easily converted into the ferrous salt, if necessary, by the action of scrap iron on its solution.

	130°.	180°.	300°.
Water	20·63	8·41	0·00
Insoluble ferric oxide.....	11·75	7·38	2·74
Soluble ferric oxide.....	18·89	29·93	40·29
Total sulphuric acid	55·10	64·38	70·93
Free sulphuric acid	20·39	9·39	0·00
Normal ferric sulphate	47·23	74·82	96·65
Ferric oxide in excess of the normal sulphate	0·00	0·00	1·63

Ferric chloride is easily obtained by the action of gaseous hydrogen chloride on burnt pyrites in the cold. The gas from the salt-cake furnace may be led into a column filled with the pyrites. Heat is developed, and the product is almost pure. C. H. B.

Dissociation of Ferric Phosphate in presence of Water and of Saline Solutions. By B. Lachowicz (*Monatsh.*, **13**, 357—370).—Investigations of the different methods for preparing ferric phosphate have shown that a salt of the composition $FePO_4$ is only occasionally obtained, the precipitated compound usually yielding, on analysis, a larger or smaller percentage of phosphoric acid than that required by this formula. Such observations, as well as the fact that the white precipitate, if left in contact with water, becomes brownish, indicate that water is in all probability able to decompose the phosphate.

The author now finds that the precipitate, containing 64·41 per cent. of PO_4 (PO_4 for $FePO_4$ = 62·91 per cent.), obtained on adding disodium hydrogen phosphate to a hot solution of ferric chloride, sufficient ammonia being present to keep the solution neutral, is only very sparingly soluble in water, but is rapidly decomposed by it. The quantity of salt decomposed by the water at any particular temperature depends on the amount of water present, and the decomposition does not proceed beyond a fixed limit, unless the phosphoric acid which has entered into solution is removed from the sphere of action. In presence of a large excess of water, the whole of the phosphoric acid is eventually withdrawn from the iron phosphate.

The presence of saline substances induces a modification in the action of water on ferric phosphate. One class of salts promotes the decomposition, another retards it, whilst a third merely acts as a solvent. Solutions of salts having an alkaline reaction have a much more powerful decomposing effect, whilst sulphates have only a slightly stronger action than pure water. The chlorides of the alkali metals appear to diminish the decomposing action of water, and cause it to behave more as a solvent towards the phosphate. Humic acid, prepared according to Mulder's instructions (*Annalen*, **36**, 243), acts on ferric phosphate as a solvent, but the greater portion of the phosphoric acid which enters into solution seems to be separated by the further decomposing action of the organic acid. G. T. M.

Nickel and Cobalt. By C. Lepierre and Lachaud (*Compt. rend.*, **115**, 115—117).—When anhydrous nickel sulphate, or the oxide,

hydroxide, or carbonate, is heated with five or six times its weight of fused ammonium sulphate, the compound $3NiSO_4,2Am_2SO_4$ separates in deep-yellow tetrahedra and cubotetrahedra, which can be rapidly washed with a small quantity of water followed by strong alcohol. In contact with water, the crystals soon become hydrated, with great development of heat.

If the preceding salt is heated in presence of ammonium sulphate, it is converted into regular octahedra of the anhydrous nickel sulphate described by Klobb; it has a canary-yellow colour, hydrates gradually in contact with water, and is insoluble in strong alcohol; sp. gr. at 20° = 3·67.

When ammonium hydrogen sulphate is employed instead of the normal salt, the nickel sulphate forms fusiform prismatic crystals, the difference being due to the presence of about 0·5 per cent. of free sulphuric acid.

The double ammonium nickel sulphate when strongly heated yields amorphous nickel oxide, but the anhydrous nickel sulphate, whether fusiform or octahedral, yields nickel oxide with the same form as the original crystals.

Cobalt sulphate behaves in a precisely similar manner, and yields a double salt with ammonium sulphate. The anhydrous sulphate occurs in both the octahedral and fusiform modifications, the difference being due to the same cause as in the case of nickel sulphate.

C. H. B.

Permolybdic Acid. By E. Péchard (*Compt. rend.*, **114**, 1481—1483).—Permolybdic acid is isolated either by decomposing the barium salt with sulphuric acid, by heating the hydrated molybdic acid, $MoO_3,2H_2O$, with a solution of hydrogen peroxide, or by the action of hydrogen peroxide on metallic molybdenum or on the blue oxide. If the solution obtained by one of these methods is evaporated in a vacuum at the ordinary temperature, it yields a yellow, crystalline powder soluble in water. The solution can be boiled without undergoing decomposition; it is not affected by strong acids, with the exception of hydrochloric acid, which reduces it to molybdic acid with evolution of chlorine. Reducing agents, such as stannous chloride and ferrous sulphate, yield first molybdic acid and afterwards the blue oxide.

Crystallised permolybdic acid has the composition $Mo_2O_7,5H_2O$. At 100° it loses $4H_2O$, and at a higher temperature it simultaneously loses both the remaining water, and also oxygen. From the composition of the permolybdates (Abstr., 1891, 988), it seems that permolybdic acid is monobasic, and hence the formula of the crystallised acid is $HMoO_4 + 2H_2O$.

When the formation of permolybdic acid is used as a test for hydrogen peroxide (Denigès), it is better to acidify with sulphuric acid than with citric acid as recommended by Crismer. Citric acid reduces permolybdic acid.

C. H. B.

Nitrogen Compounds of Platinum. By M. Vèzes (*Compt. rend.*, **115**, 44—45).—This paper contains a summary of the author's investigations of these compounds. *Potassium platomonochloronitrite*,

$Pt(NO_2)_3ClK_2 + 2H_2O$, obtained by the regulated action of hydrochloric acid on the platonitrite, is very stable in solution, and crystallises in very soluble. brilliant, pale-yellow plates. *Potassium platodichloronitrite*, $Pt(NO_2)_2Cl_2K_2$, obtained by the action of hydrochloric acid on the platonitrite, crystallises in very soluble, golden-yellow, monoclinic needles. It is the most important member of the chlorine series, because of its great stability in solution and the fact that it is constantly formed in all reactions that can give rise to nitrochloro-derivatives. *Potassium platidichloronitrite*, $Pt(NO_2)_4Cl_2K_2$, was described previously under the name *platichloronitrite*. *Potassium platitrichloronitrite*, $Pt(NO_2)_3Cl_3K_2$, is obtained by the regulated action of chlorine water on the platomonochloronitrite. It crystallises in very soluble yellow prisms, and is stable in solution. *Potassium platipentachloronitrite*, $Pt(NO_2)Cl_5K_2 + H_2O$, was previously described as a nitrosochloroplatinate, and the formula $Pt(NO)Cl_5K_2 + H_2O$ was attributed to it.

Potassium platomonobromonitrite, $Pt(NO_2)_3BrK_2$, is obtained by the regulated action of hydrobromic acid on the platonitrite. It is very stable in solution, and crystallises in very soluble, brilliant, pale-yellow plates, isomorphous with the *platomonochloronitrite*. *Potassium platodibromonitrite*, $Pt(NO_2)_2Br_2K_2 + H_2O$, was described previously under the name platobromonitrite (Abstr., 1891, 807), and the *platidibromonitrite*, $Pt(NO_2)_4Br_2K_2$ was described under the name *platibromonitrite*. *Potassium platitribromonitrite*, $Pt(NO_2)_3Br_3K_2$, was described in a previous paper as platibromonitrosonitrite, and the formula $Pt(NO)(NO_2)_2Br_3K_3$, was erroneously attributed to it. *Potassium platitetrabromonitrite*, $Pt(NO_2)_2Br_4K_2$, is obtained by the regulated action of bromine on the platonitrite; it forms red prisms which dissolve in water with partial decomposition into platinobromide, platodibromonitrite, and nitrogen oxides.

The iodine compounds are *potassium platodiiodonitrite*, $Pt(NO_2)_2I_2K_2 + 2H_2O$, described by Nilson under the name "platoiodonitrite;" *potassium platitetraiodonitrite*, $Pt(NO_2)_2I_4K_2$, previously described by the author; and *potassium platipentaiodonitrite*, $Pt(NO_2)I_5K_2$, described in a former paper under the name "nitrosoiodoplatinate," with the erroneous formula $Pt(NO)I_2K_2$.

These salts represent the following types, X being any halogen:— $Pt(NO_2)_4K_2$, $Pt(NO_2)_3XK_2$, $Pt(NO_2)_2X_2K_2$, PtX_4K_2, $Pt(NO_2)_4X_2K_2$, $Pt(NO_2)_3X_3K_2$, $Pt(NO_2)_2X_4K_2$, $Pt(NO_2)X_5K_2$, and PtX_6K_2.

C. H. B.

Chlorazopalladium Compounds. By M. Vèzes (*Compt. rend.*, **115**, 111—113).—*Potassium palladiochloronitrite*, $Pd(NO_2)_2Cl_2K_2$, analogous to the platinum compound, is easily obtained (1) by the regulated action of hydrochloric acid on potassium palladionitrite; (2) by the action of potassium nitrite on potassium palladiochloride; and (3) by the action of potassium palladiochloride on an equivalent proportion of potassium palladionitrite. It forms brownish-yellow, dichroic, monoclinic prisms of 123° 41′; $a:b:c = 0{\cdot}55041:1:0{\cdot}60334$; $\beta = 76°\ 31{\cdot}5'$. The salt dissolves in three times its weight of cold water and twice its weight of hot water, and

is very stable in solution, but when boiled with excess of chlorine or hydrochloric acid it is converted into the palladiochloride, with evolution of nitrogen oxides. The decomposition is not complete, however, until the salt has been repeatedly evaporated to dryness with the acid. An excess of potassium nitrite, on the other hand, converts the salt, on boiling, into the palladionitrite.

When dried in the air at the ordinary temperature, the crystals remain unaltered and they do not lose water at 100°. At a dull red heat nitrogen oxides are evolved, and a residue of potassium chloride and palladium is left. C. H. B.

Phosphopalladious Compounds. By E. Fink (*Compt. rend.*, **115**, 176—177).—A series of compounds analogous to Schützenberger's phosphoplatinous compounds.

Phosphopalladious chloride, $PCl_3,PdCl_2$, is prepared by heating dry, finely-divided palladium (1 atom) with phosphoric chloride (1 mol.) at 250—280° for an hour. The reddish-brown product, on recrystallisation from benzene, yields brown needles of the chloride. Phosphopalladious chloride is unstable in the air, and is decomposed by water into hydrogen chloride and an *acid* $P(OH)_3,PdCl_2$, which is obtained in yellowish-red, deliquescent crystals on evaporating the solution in a vacuum. Methyl and ethyl alcohols have a similar action, the corresponding *ethereal salts* being formed; these may be recrystallised from benzene. Phosphopalladious chloride combines in molecular proportions with phosphorous chloride; the compound crystallises from benzene in yellow, silky needles, is unstable in air, and is decomposed by water into hydrogen chloride and an acid which is under investigation. Jn. W.

Removal of Platinum from Iridium. By U. Antony (*Gazzetta*, **22**, i, 275—276).—To obtain pure iridium, the author takes metallic iridium precipitated by zinc from an acid solution of iridic chloride, treats it first with strong nitric acid (sp. gr. = 1·35) containing nitrous acid, to eliminate osmium and palladium, then repeatedly with weak aqua regia (1 part HNO_3; 3 parts HCl; 3 parts H_2O) to dissolve the platinum and any traces of osmium and palladium, washes the residues, and fuses with potassium hydrogen sulphate to remove rhodium. The insoluble iridic oxide left is reduced by hydrogen in the cold, the metal converted into potassium chloriridate, and purified by repeated crystallisation. The metal obtained in this way still contains platinum, but on passing a current of chlorine and carbon monoxide over it at a temperature of 250°, a small quantity of yellow crystals sublime, which when treated with water evolve carbonic anhydride and hydrogen chloride, and leave a black powder consisting of platinum. The iridium is left as a dark-green powder containing iridium and chlorine, and is entirely free from platinum. S. B. A. A.

Mineralogical Chemistry.

Glauber's Salt in the Potash Mines of Kalusz. By R. Zaloziecki (*Monatsh.*, **13**, 504—509).—Crystals of Glauber's salt, $Na_2SO_4 + 10H_2O$, having been discovered in a cleft of the kainite layer in the mines of Kalusz, Galicia, and the superincumbent strata being found to contain no sodium sulphate, but only sodium chloride, it was supposed that the above mentioned Glauber's salt had been formed by the action of the rain water percolating through the upper strata, where it dissolved sodium chloride, and then penetrating to the kainite layer, where the sodium sulphate is formed by the reaction between sodium chloride and the potassium sulphate of the kainite. This view was confirmed by a laboratory experiment. A 10 per cent. solution of sodium chloride was slowly filtered through a tube 30 cm. long, packed with powdered kainite, and the filtrate collected in four separate portions. The second of these deposited crystals of $Na_2SO_4 + 7H_2O$, when allowed to stand in the air, and the third crystals of $Na_2SO_4 + 10H_2O$, when concentrated on the water bath. The fourth fraction and the residue in the tube also contained sodium sulphate. It was further observed that when a solution containing calcium sulphate and much sodium sulphate is evaporated, the main portion of the calcium sulphate does not separate out until a large quantity of the sodium sulphate has crystallised. C. F. B.

Artificial Formation of Potassium Nepheline. By A. Dubois (*Compt. rend.*, **115**, 56—57).—A small quantity of potassium hydrogen fluoride is heated in a platinum crucible at first slowly and afterwards nearly to pale redness, and a small quantity of alumina is added, its solution being brought about by the addition of silica or potassium silicofluoride. The temperature of the crucible is kept constant for 15 hours, and it is then allowed to cool slowly. On treatment with water, a homogeneous and well crystallised product is left, which has the composition of potassium-nepheline,

$$K_2O,Al_2O_3,2SiO_2.$$

It forms rhombic prisms which differ entirely from sodium-nepheline in their crystalline symmetry. The prism is almost equally developed in all directions, and its angle is about 97°; it has a truncating face g' (010). The plane of the optical axes is parallel to g', and their separation is about 40°; the acute bisectrix perpendicular to p (001) is negative, and the birefractive maxima

$$N_g - N_p = 0{\cdot}008,\ N_g - N_m = 0{\cdot}002, \text{ and } N_m - N_p = 0{\cdot}006.$$

The crystals, which behave like aragonite, and group themselves in pseudo-hexagonal prisms, have a marked tendency towards hexagonal symmetry. C. H. B.

Water from the Arctic Ocean. By J. Thoulet (*Compt. rend.*, **114**, 1547—1549).—Two specimens were collected at the surface in the year 1891, and the sp. gr. and the nature and amount of the suspended matter were determined.

The first specimen was collected in lat. 68° 33′ N., and long. 12° 55′ N.W. of Paris, the depth of the sea at that point being 2048 metres, the surface temperature 6·2° and the temperature of the air 6°; sp. gr. at 6·2° compared with water at 4° = 1·0261, at 15·3° compared with water at 4° = 1·0245, and at 17·5° compared with water at 17·5° = 1·0253. The quantity of organic matter in suspension was 0·97 milligram, and of inorganic matter 0·24 milligram per litre. The latter consisted partly of rounded grains of quartz, with some mica and chalcedony.

The other specimen was collected in lat. 62° 7′ N. and long. 1° 43′ N.W. of Paris, the depth being 400 metres, and the surface temperature 12°; sp. gr. at 12° compared with water at 4° = 1·0269, at 14·2° compared with water at 4° = 1·0264, and at 17·5° compared with water at the same temperature = 1·0269. The suspended organic matter was 2·14 milligrams, and the suspended inorganic matter 0·63 milligram per litre.

The author discusses the bearing of these results on the question of ocean currents. C. H. B.

Aluminium in Mineral Waters. By F. Parmentier (*Compt. rend.*, **115**, 125—126).—The following table gives the quantity of aluminium oxide per litre in various springs:—

1.	2.	3.	4.	5.	6.	7.	8.
0·008	0·007	0·006	0·004	0·003	0·015	0·010	0·006

9.	10.	11.	12.	13.
0·001	0·014	0·006	0·002	0·009

(1) Frobert, (2) Saint Louis, No. 1, (3) Précieuse, (4) Jeanne d'Arc, (5) Sévigné, all at Vichy Saint-Yorre; (6) Dubois, (7) Vincent, both at Vichy; (8) Bayard, (9) Amélie d'Hauterive, both at Hauterive; (10) Grande Source, (11) Jeanne d'Arc, (12) Saint-Léon, all at Pougues-les-Eaux; (13) Yvonne, at Chatelguyon.

The author also detected aluminium in many cases where its presence is not recorded in previous analyses of the same springs. The precipitated alumina often contains traces of rare metals.

C. H. B.

The Mineral Water of "Monte di Malo." By P. Spica (*Gazzetta*, **22**, i, 354—371).—Chalybeate sulphuretted mineral waters containing silica, lime, manganese, and traces of arsenic arise from the side of the "Monte di Malo" (Vicenza). The water has an almost constant temperature of 15·6°. It is limpid, faintly yellowish in colour, has a slight sulphurous odour, and a pleasant taste. Its reaction is slightly acid at first, but soon becomes slightly alkaline. Its composition is as follows:—

Substances dissolved in 1 *litre at* 15·6°.

Oxygen	0·37	c.c.
Nitrogen	17·15	„
Hydrogen sulphide	1·55	„
Free carbonic anhydride	73·83	„
Carbonic anhydride (partially combined)	0·0455	gram.
„ (combined)	0·0455	„
Total residue at 110°	0·1363	„
„ at 180°	0·1265	„
Silica	0·0218	„
Titanic acid (?)	0·00103	„
Chlorine	0·000433	„
Sulphuric anhydride	0·000236	„
Phosphoric anhydride	0·002257	„
Arsenious anhydride	0·000063	„
Copper oxide	traces	
Ferric oxide	0·00798	„
Alumina	0·000836	„
Manganous oxide	0·001172	„
Baryta	traces	
Lime	0·025625	„
Magnesia	0·011338	„
Potash	0·000562	„
Soda	0·012174	„
Vanadic acid (?)	traces	

The water is entirely free from ammoniacal and nitrous compounds, but contains a little organic matter, probably of vegetable origin, which requires for its oxidation a quantity of permanganate equivalent to 0·00144 gram of oxygen per litre of water. S. B. A. A.

Alteration of Chalybeate Mineral Waters. By J. Riban (*Compt. rend.*, **114**, 1483—1485).—Some time ago the author estimated the quantity of iron held in solution in various bottled mineral waters, as sold by pharmacists. His results are given in the following table, together with the quantity of iron per litre originally in solution when the water issued from the spring:—

	1.	2.	3.	4.	5.	6.
In solution as protoxide	0·0007	0·0000	0·0000	0·0002	—	0·0000
Total iron in solution	0·0022	0·0007	0·0007	0·0010	0·0059	0·0011
Iron originally in solution	0·0809	0·0082 0·0041	0·0521	0·0171	0·0050	0·0618

	7.	8.	9.	10.	11.	12.	13.
In solution as protoxide ..	0·0000	0·0004	0·0000	0·0255	0·0002	0·0002	0·0004
Total iron in solution ...	0·0004	0·0015	0·0000	0·0260	0·0015	0·0013	0·0011
Iron originally in solution..	0·0618	0·0072 / 0·0021	0·0112	0·0448	?	?	0·0073

(1) Auteuil; (2) Bussang, the two numbers given for the original quantity of iron being by two different authorities; (3) Forges (Royale); (4) Forges (Reinette); (5) Lamalou (Bourges); (6) Orezza (Sorgenta sottana); (7) the same; (8) Pougues (Saint Légér), the two numbers for the total iron being from two authorities; (9) Soultzbach; (10) Spa (Pouhon); (11) Vals (Rigolette); (12) Vals (Dominique); (13) Vichy (Lardy). C. H. B.

Chalybeate Mineral Waters. By F. Parmentier (*Compt. rend*, **115**, 53—55).—The author quotes analyses which show that chalybeate waters retain a considerable quantity of iron in solution, if bottled whilst they contain carbonic anhydride (compare Riban, preceding abstract). C. H. B.

Chalybeate Mineral Waters. By J. Riban (*Compt. rend.*, **115**, 185).—A reply to Parmentier (preceding abstract).

Organic Chemistry.

Affinity Coefficients of Alkyl Iodides and Bromides. By N. Menschutkin and M. Vasileff (*J. Russ. Chem. Soc.*, **22**, 346—358; also *Zeit. physikal. Chem.*, **5**, 589—600).—The rates at which alkyl iodides or bromides combine directly with organic amines give a measure of the affinity of both these classes of substances. In this paper, the authors communicate the results of their investigations of the rate of combination of the iodides and bromides of the alcohol radicles with triethylamine. The alkyl chlorides do not unite with triethylamine under the conditions of experiment chosen by the authors. Triethylamine and the alkyl halides were mixed in molecular proportions, and 1 vol. of the mixture was diluted with 15 vols. of acetone or of benzene. Small glass tubes were filled with weighed quantities of this mixture, and these were immersed for a definite time in a thermostat at 100°. On being taken out, they were rapidly cooled with ice-water, and the quantity of the bromide or iodide of the ammonium base they contained was at once determined, after neutralisation with dilute nitric acid, by titration with silver nitrate

solution, potassium chromate being used as indicator. The results with iodides were not quite sharp, as the combination goes on in aqueous solution, even at the ordinary temperature. From the observed times and the titres, the coefficient of velocity of the reaction was calculated by the usual formula.

In acetone solution, the combination proceeds about 10 times as fast as in benzene solution, and the coefficients of velocity of the iodides are from six to seven times as great as those of the corresponding bromides. The coefficients diminish as the molecular weight of the normal alkyls increases, and are greater for normal than for iso-alkyls. The following table contains the numerical values of the coefficient of velocity, k:—

	Iodides.		Bromides in acetone.
	In benzene.	In acetone.	
Methyl	0·665	—	—
Ethyl	0·00584	0·0608	0·00958
Normal propyl	0·000984	0·0116	0·00165
Isopropyl	—	0·00121	—
Normal butyl	—	0·00832	0·00123
Isobutyl	—	0·00191	0·000252
Normal heptyl	—	0·00653	0·00119
Normal octyl	—	0·00602	0·00110

The ratios of the coefficients of the alkyls agree well with those obtained by Conrad and Hecht from the action of sodium ethoxide and alkyl iodide at 24°. J. W.

Action of Methyl Iodide and of Chloroform on Nitroisopropane. By I. Kisel (*J. Russ. Chem. Soc.*, **22**, 380—383).—Caustic soda (2 mols.) dissolved in alcohol was added to nitroisopropane (1 mol.), and the sodium compound thus obtained was heated with methyl iodide (3 mols.) in a sealed tube at 110° for two hours. Sodium iodide and small quantities of a hygroscopic substance separated out from the alcoholic solution on cooling. On distilling the liquid portion, alcohol passed over, together with excess of methyl iodide and two liquids of unknown composition. The solid residue was treated with strong caustic soda and the solution distilled. Propylamine and ammonia came over, with another base, whose chloride could not be crystallised. From the mother liquor from which ammonium and propylammonium chloride were crystallised, two different sorts of crystals (nodules and plates) were obtained by evaporation in a vacuum and recrystallisation from cold alcohol. The substance forming nodular masses contained a quantity of chlorine corresponding with the formula $NHMe{\cdot}OH,HCl$.

When chloroform was employed instead of methyl iodide, a substance was obtained which crystallised in rhombic plates, was easily

soluble in alcohol and ether, and had approximately the composition $C_3H_6NO_2$. Aldehyde was observed among the products when ethyl iodide was used. J. W.

Polymerides of Dichloracetonitrile and Trichloracetonitrile. By N. Tscherven-Iwanoff (*J. pr. Chem.* [2], **46**, 142—151; compare Abstr., 1886, 323; 1891, 1332).—Dihydroxyperchloromethylcyanidine (Abstr., 1891, 1332) crystallises in needles, melts at 152—153°, and dissolves easily in water, sparingly in glacial acetic acid, but not in the other usual solvents; it forms unstable salts. Amidodimethylcyanidine (*loc. cit.*) dissolves easily in water and glacial acetic acid, but not in alcohol or ether.

Dichloracetonitrile is polymerised somewhat more easily by hydrogen bromide than by hydrogen chloride (Abstr., 1885, 739); its *hydrochloride* melts with decomposition at 140—145°, and is converted into the polymeride and hydrogen chloride when heated in a sealed tube at 130—140°. As hydrogen iodide acts on these nitriles, it cannot be used for their polymerisation.

Determinations of the molecular weights of these polymerides by Raoult's method give results which agree with the formulæ $(CCl_3{\cdot}CN)_3$ and $(CHCl_2{\cdot}CN)_2$ respectively. A. G. B.

Carbon Diiodide. By H. Moissan (*Compt. rend.*, **115**, 152—155).—When carbon tetriodide, CI_4 (Abstr., 1891, 1420), is exposed in a vacuum to the sun's rays, or even to diffused daylight, or to a temperature of 120°, it splits up into iodine and carbon diiodide, C_2I_4. The diiodide is, however, best prepared by gradually adding the theoretical quantity of powdered silver to a cooled solution of the tetriodide in carbon tetrachloride (or bisulphide), then sealing up the tube, and allowing the reaction to proceed in the cold until the red colour of the tetriodide has changed to the yellow colour of the diiodide. Excess of silver at a higher temperature (50°) causes the complete reduction of the tetriodide. The solution of the diiodide is then separated from the silver iodide, the solvent distilled off on the water-bath, the residue allowed to crystallise, and the crystals purified, either by recrystallisation, or by sublimation in a vacuum.

Carbon diiodide crystallises from carbon tetrachloride in brilliant, pale yellow needles, and from boiling alcohol in small, brilliant prisms. It melts at 185°, volatilises without decomposition at a slightly higher temperature, but begins to decompose at 200°. Its sp. gr. is 4·38. It is very soluble in carbon tetrachloride, carbon bisulphide, ether, and boiling alcohol, but only sparingly in cold alcohol. It is not reduced by hydrogen, even at 200°, and is not attacked by chlorine or bromine in the cold, although at higher temperatures these effect a partial substitution of the iodine. When heated in oxygen, it melts, and then splits up into its elements, the carbon burning to carbonic anhydride. It is not attacked by sulphur below 110°, but at that temperature the iodine is displaced by sulphur, carbon bisulphide being formed. Phosphorus attacks it at a temperature somewhat above the melting point of that element. It is not acted on by weak boiling solutions of potassium permanganate or

chromic acid, or by boiling nitric acid, although it is completely oxidised by the latter at 180°. It is decomposed by sulphuric acid at 250°, but not by hydrochloric or hydriodic acid. It is not affected by boiling aqueous potash, but is decomposed into iodoform, iodine, and potassium carbonate by fusion with solid potash. Silver fluoride does not act on a solution of the iodide in carbon tetrachloride.

Jn. W.

Action of Chlorine on Isobutyl Alcohol. By A. Brochet (*Compt. rend.*, **114**, 1538—1541).—When isobutyl alcohol is treated with a current of dry chlorine, there is at first considerable development of heat, but after a time the reaction slackens and the liquid must be gently heated. No isobutyl chloride is formed, and the product can be separated into two fractions, boiling respectively at 80—100° and 170—250°. The examination of the latter is not yet complete; the former consists of *chlorisobutaldehyde*, $CMe_2Cl{\cdot}COH$. It boils at 90—91°, and has an odour recalling that of chloral, and a piquant, bitter taste; sp. gr. at 15°, compared with water at 4°, = 1·086. It reduces Fehling's solution and ammoniacal silver nitrate, combines with sodium hydrogen sulphite to form a crystalline compound, and, when oxidised with dilute alkaline permanganate, yields acetone and hydroxyisobutyric acid,

$$CMe_2(OH){\cdot}COOH,$$

melting at 78°.

Chlorisobutaldehyde does not solidify at −20°, and yields no hydrate at this temperature. When agitated for a short time with its own volume of concentrated sulphuric acid, it forms slender needles, which can be purified by washing, followed by distillation in water vapour. This product is further purified by solution in acetic acid, precipitation with water, and redistillation. It forms white, odourless, tasteless needles, which melt at 107°, sublime at 110°, and are volatile in water vapour, even below 100°. This compound is a polymeride of monochlorisobutaldehyde, and the freezing point of its acetic acid solution shows that it has the formula $C_{12}H_{21}Cl_3O_3$. It is soluble in ether, alcohol, acetic acid, benzene, &c., and crystallises from ether in monoclinic prisms; it reduces Fehling's solution and ammoniacal silver nitrate distinctly, although with some difficulty.

C. H. B.

Pentamethylene Glycol and its Oxides. By N. Demyanoff (*J. Russ. Chem. Soc.*, **22**, 388—391).—Pentamethylene glycol is a thick liquid with a burning taste, and does not solidify in a mixture of snow and salt. It mixes freely with water and alcohol, but is only soluble with difficulty in ether. At a pressure of 31 mm., it distils at 162°. Its density is $d\ 0°/0° = 1·0041$; and its vapour density corresponds with the formula $C_5H_{12}O_2$. When heated with three times its volume of 60 per cent. sulphuric acid in a sealed tube at 100° for $1\frac{1}{2}$ hours, it became brown, and a quantity of tarry matter was formed; the product, diluted with its own bulk of water, and distilled on the water bath, yielded a distillate which separated into two layers. After neutralisation of the whole with potash, the upper

layer was separated and dried with fused caustic potash. On a first distillation, it boiled between 79° and 83°; on refractionation, it came over between 80° and 81°. The product is a light, colourless, mobile liquid, with an odour resembling that of ethyl ether. Analyses and vapour density determinations agree with the formula $C_5H_{10}O$. It is, therefore, the anhydride of pentamethylene glycol. Its density at $0°/0° = 0·8800$, and in its properties it is very similar to the isomeric oxide of γ-pentylene glycol. It is more soluble in cold than in boiling water, and is miscible with alcohol and ether. It does not combine with water, even on heating the two together at 200°, but it unites readily at 100° with fuming hydrobromic acid. Neither silver nitrate in ammoniacal solution, nor Fehling's solution, is reduced by it. Hydroxylamine has no action on it. Its formula is probably

$$\begin{matrix} CH_2\cdot CH_2\cdot O \\ | \qquad\quad | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}$$

J. W.

Action of Zinc Dust and Alcohol on Chlor-α-dibromhydrin. By G. Gustavson (*J. pr. Chem.* [2], **46**, 157—160; compare Abstr., 1891, 159, 888).—The chlor-α-dibromhydrin was dissolved in alcohol, and the solution dropped on to the zinc kept at 90° in an apparatus from which both gaseous and liquid products could be collected. These were recognised as consisting almost entirely of propylene and allyl chloride. The former is frequently formed by the action of zinc dust and alcohol on halogen glycerol derivatives; the latter is regarded by the author as being evidence that chlorotrimethylene is the first product of the reaction. In support of this point, he adduces the conversion of chlorotrimethylene into allyl acetate, by the action of potassium acetate and acetic acid.

A. G. B.

Action of Acetic Anhydride on Glucose. By Istrati and Edeleanu (*Chem. Centr.*, 1892, i, 624; from *Bull. Soc. Sci. Fiz. Bucuresci*, **1**, 46).—According to the authors, V. Meyer's aldehyde formula, $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot COH$, for glucose, cannot be correct, because no unsaturated hexabasic acid is obtained when this sugar is heated with acetic anhydride for several days, the only product of the reaction being the tetracetyl derivative. A. G. B.

Sugar from Linseed. By R. W. Bauer (*Landw. Versuchs-Stat.*, **40**, 480).—Crude linseed mucilage, which had been treated with alcohol and ether, was boiled with dilute sulphuric acid, and the filtrate treated with chalk, evaporated down, and extracted with alcohol. The sugar so obtained is dextrorotatory, $[\alpha]_D = +46·135°$. The phenylhydrazine reaction gave a slightly lævorotatory yellow solution, and needles of the dextrosazone melting at 204°. N. H. M.

Isomaltose. By C. J. Lintner (*Chem. Centr.*, 1892, i, 623; from *Woch. Brauerei*, **9**, 245—247).—The author replies to some criticisms passed by the *Brewing Trade Review*, **6**, 52, on his isomaltose. The assertion, made in the Review in question, that the substance termed isomaltose by E. Fischer and others is identical with the substance formerly called gallisin, the author says, is incorrect. Moreover, gal-

lisin must be expunged from chemical literature. The preparation of the osazone of the author's isomaltose proves, beyond a doubt, the identity of this substance with Fischer's isomaltose. Moreover, he believes that the maltodextrin theory of Brown and Morris (Trans., 1885, 570) is not tenable; the transformation products of starch are by no means so numerous as they make out, and are probably limited to three, namely, dextrin, isomaltose, and maltose. The author's method for isolating isomaltose will be divulged later; it differs from that employed by Brown and Morris for preparing maltose.

A. G. B.

Precipitation of Raffinose by Ammoniacal Lead Acetate. By T. Koydl (*Chem. Centr.*, 1892, i, 653—654; from *Österr.-ungar. Zeit. Zuck.-ind.*, **21**, 92—93).—The author has previously shown that although ammoniacal lead acetate is a good qualitative precipitant for raffinose, it is of no use for quantitative separation, inasmuch as the precipitation is never complete. Weisberg having maintained that quantitative separation is possible by means of this reagent, the author adduces new experiments to prove that Weisberg is in error.

A. G. B.

Vegetable Cholesterol. By Gérard (*Compt. rend.*, **114**, 1544—1546).—The cholesterol derived from phanerogamous plants is identical in physical and chemical properties with the phytosterin of Hesse, whilst that derived from cryptogams gives the same reactions as the ergosterin of Tanret.

In order to obtain a pure product, the crude material is treated with dry ether, the residue from the distillation of the ethereal solution is saponified with alcoholic potash, and the soap is dried and extracted with ether. The ethereal solution, on evaporation, deposits acicular crystals which are purified by further treatment with potash. The whole is then dissolved in water, and the strongly alkaline liquid is agitated with chloroform, when the cholesterol separates in almost pure crystals. Final purification is effected by converting the cholesterol into the benzoate, crystallising the latter repeatedly from alcohol, and saponifying.

Cholesterol from the higher plants has the following melting points and rotatory power:—

	Rotatory power.	Melting point.
Dried in a vacuum....	$\alpha_0 = -34{\cdot}4°$	132—133°
Dried at 100°	$\alpha_0 = -36{\cdot}5°$	135°

The numbers are identical with those obtained by Hesse for phytosterin. Although the cholesterols from lower vegetables all give the reactions of ergosterin, the melting point and rotatory power vary in some cases:—

	Rotatory power.	Melting point.
From *Penicillium glaucum*, dried at 100°	$\alpha_D = -143{\cdot}3°$	135·0°
,, *Æthalium septicum*, dried at 100°	$\alpha_D = -28{\cdot}0°$	134·5°

C. H. B.

Action of Propyl Iodide on Trimethylamine. Trimethylpropylammonium Iodide. By H. Malbot and A. Malbot (*Bull. Soc. Chim* [3], **7**, 136).—Trimethylamine in aqueous solution is

allowed to act in molecular proportion on propyl iodide for 18 hours; the action is complete when a little of the product poured into potash gives a precipitate which melts on heating the solution, solidifies again on cooling, and dissolves on dilution. The main bulk of the product is evaporated to dryness to expel trimethylamine, taken up with water, the solution shaken with the calculated quantity of silver oxide, and filtered. After concentrating and adding hydrochloric acid and platinum tetrachloride, the solution yields *trimethylpropylammonium platinochloride*, which may be crystallised from water, and is very stable towards heat. W. J. P.

Action of Isopropyl Iodide on Trimethylamine. Trimethylisopropylammonium Iodide. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **7**, 136—138).—The action of isopropyl iodide on trimethylamine is exactly similar to that of the normal iodide (see preceding abstract). The reaction is completed after five days' contact in the cold, and only proceeds a little more rapidly at 100°; a small quantity of propylene is liberated, probably owing to the presence of a little propylene iodide. *Trimethylisopropylammonium iodide* is thus obtained in beautiful crystals which are more soluble than those of the corresponding normal propyl derivative. The *platinochloride* crystallises in long, red, hydrated prisms which lose water in the desiccator. W. J. P.

Action of Allyl Iodide on Trimethylamine. Trimethylallylammonium Iodide. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **7**, 138—139).—The reaction between trimethylamine and allyl iodide is very violent, slight explosions occurring as the amine falls, drop by drop, into the iodide. *Trimethylallylammonium iodide* is isolated in a similar manner to the corresponding compounds already described by the authors (see preceding abstracts). The *platinochloride* is very stable towards heat. W. J. P.

Nitroguanidine and Amidoguanidine. By J. Thiele (*Annalen*, **270**, 1—63).—The author's experiments have shown that Jousselin's "nitrosoguanidine" (Abstr., 1878, 132; 1879, 613 and 914) is in reality nitroguanidine, and that its constitution is most probably represented by the formula $NO_2 \cdot NH \cdot C(NH) \cdot NH_2$ (compare Pellizzari, this vol., p. 579).

Nitroguanidine melts at 230° with evolution of ammonia, and is soluble in 372 to 375 parts of water at 19·3°, and in about 11 parts of boiling water. The *silver* derivative, $CH_3N_4O_2Ag$, is precipitated when barium hydroxide is gradually added to a warm aqueous solution containing nitroguanidine and silver nitrate in molecular proportion; it is a colourless compound, almost insoluble in water, but readily soluble in acids, ammonia, and ammonium salts; it separates from a hot solution of ammonium nitrate in microscopic needles. It turns yellow when treated with alkalis, and darkens on exposure to the air or on prolonged washing with water; it has an alkaline reaction, and explodes when heated. A yellow precipitate, which seems to have the composition $CH_2N_4O_2Ag_2$, is formed when soda or

barium hydroxide is added to a solution of nitroguanidine in ammoniacal silver nitrate; it is very hygroscopic, and decomposes very readily when dried at a moderate temperature. The *nitrate*, $CH_4N_4O_2,HNO_3$, crystallises from hot concentrated nitric acid in nacreous plates, and melts at 147°. The *hydrochloride*, $CH_4N_4O_2,HCl$, crystallises in plates or prisms. When nitroguanidine is treated with soda and zinc-dust, and then with a solution of a ferrous salt, a beautiful red coloration is produced; attempts to prepare alkyl and acidyl derivatives of nitroguanidine were unsuccessful.

Amidoguanidine hydrochloride, $NH_2{\cdot}NH{\cdot}C(NH){\cdot}NH_2,HCl$, can be obtained by gradually adding glacial acetic acid (124 grams) diluted with an equal volume of water, to a mixture of nitroguanidine (208 grams) and zinc-dust (700 grams) which has been previously rubbed to a thick paste with ice and water; during the addition of the acid, which occupies 2—3 minutes, the mixture is constantly stirred, and the temperature kept at 0° by adding ice. The temperature of the mixture is then allowed to rise slowly to 40—45°, and, as soon as a portion gives no coloration with soda and a ferrous salt, reduction is at an end; the filtered solution is then mixed with excess of hydrochloric acid, concentrated on the water-bath, taken up with alcohol, and evaporated to dryness; the residue consists of amidoguanidine hydrochloride, guanidine hydrochloride, and a little ammonium chloride, which are separated by means of alcohol. Amidoguanidine hydrochloride crystallises from dilute alcohol in large, thick prisms, melts at 163°, and is very readily soluble in water, but insoluble in ether; its physiological action is similar to that of guanidine and methylguanidine. The *platinochloride*, $(CH_6N_4)_2,H_2PtCl_6$, is a yellow substance melting at 145—146°. The *nitrate*, CH_6N_4,HNO_3, crystallises from water in large plates, from alcohol in needles, and melts at 144°; it is only sparingly soluble (12·01 parts in 100) in water at 15·9°. The *sulphate*, $(CH_6N_4)_2,H_2SO_4 + H_2O$, crystallises in needles, loses its water at 110°, and melts at 207—208° with decomposition; it is very readily soluble in water, but insoluble in alcohol. The *acid sulphate*, CH_6N_4,H_2SO_4, crystallises from water, in which it is only sparingly soluble, in small, yellow needles. When a solution of the sulphate is treated with the theoretical quantity of barium hydroxide, a solution of amidoguanidine is obtained; this solution gradually turns reddish on exposure to the air, and decomposes, with evolution of ammonia, when evaporated at a moderate temperature; on evaporation under reduced pressure, it yields a reddish, crystalline substance which has an alkaline reaction, and is soluble in alcohol, but insoluble in ether.

A compound of the composition $(CH_5N_4)_2Cu,2HNO_3$, is obtained as a violet, crystalline precipitate when a solution of amidoguanidine nitrate is treated with copper nitrate and sodium acetate; it crystallises in microscopic plates or prisms, and is only very sparingly soluble in cold water, yielding a violet solution; it is decomposed by boiling water with separation of copper, and also by ammonia and nitric acid. The corresponding *sulphate*, $(CH_5N_4)_2Cu,H_2SO_4$, prepared in like manner, is a violet, crystalline, sparingly soluble powder.

Acetylamidoguanidine nitrate, $C_3H_8N_4O,HNO_3 + H_2O$, is formed when amidoguanidine nitrate is heated with acetic acid and a few drops of nitric acid; it separates from water in large crystals which melt at 85—90°, and are readily soluble in water, but only sparingly in alcohol; these crystals lose their water at 55—60°, the anhydrous substance melting at 142—143° with decomposition. The *picrate*, $C_3H_8N_4O,C_6H_3N_3O_7$, crystallises from water in yellow needles.

When amidoguanidine is treated with dilute acids, or with caustic alkalis, it is first converted into semicarbazide with liberation of ammonia; the semicarbazide then undergoes decomposition into carbonic anhydride, ammonia, and hydrazine, identical with the compound described by Curtius.

Benzalsemicarbazide, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, is obtained, together with benzalazine (compare Curtius and Jay, Abstr., 1891, 393), when an acid solution of the decomposition products of amidoguanidine is treated with benzaldehyde; it crystallises from water and alcohol in small, lustrous plates, melts at 214—220° with decomposition, and is moderately easily soluble in alcohol, but only sparingly in boiling water, and insoluble in cold ether.

Benzalamidoguanidine, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}N{:}CHPh$, is precipitated in lustrous plates, when an aqueous solution of an amidoguanidine salt is treated with benzaldehyde and excess of concentrated potash; it melts at 178°, and is readily soluble in hot water and alcohol, but only sparingly in boiling benzene; its aqueous solution has an alkaline reaction, and gives precipitates with solutions of the heavy metals. The *hydrochloride*, $C_8H_{10}N_4,HCl + 3H_2O$, is deposited in colourless needles when hydrochloric acid is added to an aqueous solution of the base; it melts in its water of crystallisation when heated to about 50°, loses its water when kept under reduced pressure, and dissolves freely in water and alcohol; its aqueous solution gives, with mercuric chloride, a precipitate which is only sparingly soluble in cold water. The *aurochloride*, $C_8H_{10}N_4,HAuCl_4$, crystallises in slender, reddish-yellow needles, melts at 194°, and is only sparingly soluble in boiling water, by which it is decomposed. The *platinochloride*, $(C_8H_{10}N_4)_2,H_2PtCl_6 + 2H_2O$, crystallises in small needles, and melts at 208° when heated slowly. The *nitrate*, $C_8H_{10}N_4,HNO_3$, separates from boiling water in granular masses, melts at 158°, and is only sparingly soluble in cold water. The *nitrite*, $C_8H_{10}N_4,HNO_2$, crystallises from a mixture of chloroform and alcohol in colourless plates, melts at 137°, and turns brown on exposure to light; it is very readily soluble in water and alcohol.

Azodicarbonamidine nitrate, $NH_2{\cdot}C(NH){\cdot}N{:}N{\cdot}C(NH){\cdot}NH_2,2HNO_3$, is obtained as a yellow precipitate when a cold, saturated solution of potassium permanganate is gradually added to a solution of amidoguanidine nitrate in normal nitric acid. It is an intensely yellow, crystalline powder, explodes at 180—184° without melting, and is insoluble in alcohol and ether, and only very sparingly soluble in cold water; it dissolves in warm water and in alkalis, yielding intensely yellow solutions which undergo decomposition on boiling. With ammoniacal silver nitrate, it gives an orange-red, and with ammoniacal copper solutions, a brownish-black precipitate. The

picrate crystallises from warm water in orange-red plates, melts at 179—180° with decomposition, and is only sparingly soluble in hot water, by which it is decomposed.

Hydrazodicarbonamidine nitrate,

$$NH_2{\cdot}C(NH){\cdot}NH{\cdot}NH{\cdot}C(NH){\cdot}NH_2,2HNO_3 + H_2O,$$

is formed when the preceding compound is treated with the ordinary reducing agents, and is best prepared by passing hydrogen sulphide into water containing the nitrate in suspension; it separates from water in large, lustrous crystals, melts at 138° with sudden decomposition, and is sparingly soluble in alcohol; it loses its water under reduced pressure, and then melts at 132° with previous decomposition when quickly heated.

Azodicarbonamide, $NH_2{\cdot}CO{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, is obtained, together with ammonium nitrate and a very small quantity of a sparingly soluble, colourless compound, when hydrazodicarbonamidine nitrate is boiled with water for 10—15 minutes; it is an orange-red, crystalline powder, very sparingly soluble in hot water, and insoluble in alcohol and cold water. When heated at 180—200°, it turns white, with evolution of ammonia, and the residue consists principally of cyanuric acid; when treated with phenol and concentrated sulphuric acid successively, there is produced a dark-green coloration which becomes yellow on diluting, and green again on adding alkali.

Hydrazodicarbonamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, is formed when the azo-compound is reduced with hydrogen sulphide in boiling aqueous solution, or boiled with concentrated hydrochloric acid; it can also be prepared by treating hydrazine sulphate with potassium cyanate in aqueous solution. It crystallises from water in colourless, microscopic plates, melts at 244—245° with decomposition, and is insoluble in alcohol and ether, and only very sparingly soluble in boiling water; it reduces ammoniacal silver solutions.

Diazoguanidine nitrate, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}N{:}N{\cdot}NO_3$, is best prepared by adding sodium nitrite to a nitric acid solution of amidoguanidine nitrate, the temperature being kept below 40°; it crystallises from boiling alcohol in plates or prisms, melts at 129°, and is readily soluble in water and alcohol, but insoluble in ether. Its aqueous solution is stable at the ordinary temperature, as is also the dry diazo-compound; on treatment with hydrogen sulphide, it is converted into guanidine. The *hydrochloride* forms large plates. The *picrate*, $CH_4N_5,C_6H_3N_3O_7$, crystallises in small, yellow needles, and is very sparingly soluble in water.

When amidoguanidine nitrate is treated with sodium nitrite in acetic acid solution, there is precipitated a yellow, amorphous, explosive substance which has the composition $C_2H_6N_{10}O$.

When a solution of diazoguanidine nitrate is treated with an ammoniacal solution of silver nitrate, a yellow precipitate is produced, and, on acidifying the filtrate with dilute nitric acid, a small quantity of silver nitride is thrown down; the yellow precipitate has the composition CN_5Ag_3, and is probably a molecular compound of silver cyanamide and silver nitride; when treated with dilute nitric acid, silver nitride remains undissolved, and silver nitrate and cyanamide

pass into solution. When an ammoniacal solution of copper sulphate is added to a solution of a diazoguanidine salt, a dark-brown precipitate of copper cyanamide, mixed with a little copper amidotetrazotate, is produced, and the filtrate contains a large quantity of hydrogen nitride.

Diazoguanidine salts are decomposed by alkalis, yielding cyanamide and hydrogen nitride; this reaction can be conveniently employed for the preparation of the last-named compound.

Amidotetrazotic acid, $\begin{matrix}N—N\\ \|\\ N\cdot NH\end{matrix}\!\!>\!C\cdot NH_2$, is formed, together with hydrogen nitride, when diazoguanidine salts are boiled with dilute acids; when acetates or carbonates are employed, instead of dilute acids, amidotetrazotic acid is the sole product. It crystallises from water in lustrous plates or prisms which contain 1 mol. H_2O, and melt at 203° (corr.); it is soluble in 82·25 parts of water at 18·4°, and dissolves freely in hot water, but is only sparingly soluble in alcohol, and insoluble in ether. It seems to be completely decomposed by potassium permanganate in alkaline solution; aqueous solutions of the acid give precipitates with solutions of cupric, mercuric, and mercurous salts. The *sodium* salt, $CH_2N_5Na + 3H_2O$, prepared by treating the acid with sodium carbonate, crystallises in large prisms, is readily soluble in water, and is decomposed by acetic acid. The *barium* salt, $(CH_2N_5)_2Ba$, separates from hot dilute alcohol in needles which seem to contain 5 mols. H_2O. The *silver* salt, CH_2N_5Ag, is stable in the light, but explodes when heated; it is only very sparingly soluble in warm nitric acid. The *hydrochloride*, $CH_3N_5,HCl + H_2O$, is deposited in prisms when the acid is dissolved in warm, concentrated hydrochloric acid, and the solution allowed to cool; it loses its water under reduced pressure, and is reconverted into amidotetrazotic acid when heated at 95—100°, or when treated with water.

When sodium amidotetrazotate is treated with sodium nitrite and dilute hydrochloric acid in the cold, diazotetrazole is formed; this compound cannot be isolated on account of its instability. Moderately concentrated solutions explode even at 0° after a few seconds, and more dilute solutions gradually decompose on keeping.

Tetrazoleazodimethylaniline, $CN_4H\cdot N:N\cdot C_6H_4\cdot NMe_2$, is precipitated when dilute solutions of dimethylaniline and sodium acetate are added to a dilute solution of diazotetrazole; it crystallises from alcohol in red plates, begins to decompose at 150°, explodes at about 155°, and is only sparingly soluble in water and ether. The *hydrochloride* is a brownish-green compound, and is decomposed by water. The *sodium* derivative crystallises from water in small, red, lustrous octahedra, and from soda, in which it is more sparingly soluble, in needles, very similar in appearance to the crystals of chromic acid.

Tetrazoleazo-β-naphthylamine, $CN_4H\cdot N:N\cdot C_{10}H_6\cdot NH_2$, prepared in like manner, separates from alcohol in the form of a lustrous, green powder, melts at about 184°, and is readily soluble in soda, but only sparingly in alcohol, and almost insoluble in water.

F. S. K.

Supposed Reaction of Spermine. By Duclaux (*Compt. rend.*, **115**, 155—157).—The increased rate of decomposition of water by magnesium and gold chloride attributed by Poehl to the chemical action of spermine is due to physical action, the spermine causing a froth, and thus exposing a large surface to the action of the magnesium-gold couple. Other substances of a similar nature, such as soapy water, saponin, panamin, and egg-albumin, have the same effect. The same amount of hydrogen and magnesia, moreover, are ultimately formed in the absence of froth-producing material. Jn. W.

Action of Zinc and Ethyl Monochloracetate on the Aldehydes. By S. Reformatsky (*J. Russ. Chem. Soc.*, **22**, 194—208).—The analogy between the ketones and aldehydes renders it probable that the latter by the action of zinc and ethyl monochloracetate should yield β-hydroxy-acids. Experiments made in this direction have, however, not confirmed the supposition. On heating ethaldehyde with zinc and ethyl monochloracetate, a very small amount of hydroxy-acid seems to be formed; this, however, the author attributes to secondary reactions. Experiments with propaldehyde did not yield hydroxyvaleric acid, but a mixture of propionic acid with glycollic acid, and a neutral product. Analysis of the latter gave numbers which corresponded most closely with the formula $C_{10}H_{20}O_3$, but the author thinks the true formula must be $(C_3H_6O)_3$. As this compound is entirely different in its properties from aldol, the author comes to the conclusion that it must be a polymeride of propaldehyde, and probably an analogue of paraldehyde. The conclusion that it contains no aldehyde groups was confirmed by the negative results obtained on treating it with rosaniline and hydroxylamine. On distilling it with a drop of sulphuric acid, it was changed into propaldehyde, just as paraldehyde is into ethaldehyde. Vapour density determinations by V. Meyer's method in toluidine vapour gave the numbers 6·36, 6·63; in naphthalene vapour, 5·95; the theoretical number is 6·02.

The author calls the compound parapropaldehyde; it is a mobile liquid boiling at 169—170° (768 mm.), insoluble in water, easily soluble in alcohol and ether. It could not be solidified in a freezing mixture of snow and concentrated hydrochloric acid.

The author thinks that a compound $COOEt{\cdot}CH_2{\cdot}ZnCl$ is formed as an intermediate product in the reaction. The action of zinc chloride alone does not yield parapropaldehyde.

The action of zinc and ethyl monochloracetate on isobutaldehyde yielded no hydroxy-acid; isobutyric and formic acids were formed, and the sodium salts crystallised out together in the proportion of 3 to 1 from an alcoholic solution; besides these, a neutral compound which gave a violet colour with rosaniline was also produced, but was not further investigated.

The action of zinc and ethyl monochloracetate on œnanthol yielded œnanthylic acid and a dark-coloured neutral product, which was not investigated.

Benzaldehyde similarly treated yielded benzoic acid. M. F.

Action of Iodine on the Silver Salts of Fatty Acids. By A. Simonini (*Monatsh.*, **13**, 320—325).—The author has repeated the experiments of Birnbaum (*Annalen*, **152**, 111), who states that he obtained silver iodide, carbonic anhydride, acetic acid, methyl acetate, hydrogen, and acetylene by the action of iodine on silver acetate, and finds that, when heated together at 130—140°, the substances yield only the four products first named. Neither hydrogen nor any unsaturated hydrocarbon is formed, and the yield of methyl acetate is about 50 per cent. of that required by the equation $2CH_3{\cdot}COOAg + I_2 = 2AgI + CO_2 + CH_3{\cdot}COOMe$.

Iodine and silver caproate, when heated together at about 100°, behave in a precisely similar way, forming silver iodide, carbonic anhydride, and normal amyl caproate, the yield of the last-named being about 75 per cent. of that corresponding with the equation $2AgC_6H_{11}O_2 + I_2 = C_5H_{11}{\cdot}C_6H_{11}O_2 + CO_2 + 2AgI$. G. T. M.

An Additive Compound of Hydrogen Cyanide with Ethyl α-Cyanopropionate. By N. Zelinsky and A. Buitchichin (*J. Russ. Chem. Soc.*, **22**, 169—171).—It has been previously observed (Abstr., 1889, 377) that when potassium cyanide acts on ethyl α-bromopropionate, besides the two compounds ordinarily obtained (ethyl α-cyanopropionate and a condensed product, the ethyl salt of symmetrical dimethylcyanosuccinic acid), a third crystalline nitrogenous substance is formed. The supposition then made, that this product is an additive product of hydrogen cyanide with ethyl α-cyanopropionate, has been confirmed by analysis as well as synthetically.

By the action of a strong solution of sodium or potassium hydroxide, it is easily dissolved in the cold with considerable development of heat, and if this solution is acidified with hydrochloric acid and distilled in a current of steam, a considerable quantity of hydrocyanic acid passes over. If, however, water is added to the potash solution and the mixture is heated, ammonia is given off. On heating the solution until ammonia ceases to be evolved, acidifying with hydrochloric acid, extracting with ether, and evaporating the ethereal solution, a crystalline, organic acid is left which melts at 130°, the melting point of isosuccinic acid. Its silver salt, dried at 115° to 120°, was analysed, and gave results corresponding with the formula $C_4H_4O_4Ag_2$. The analysis of the additive compound corresponds with the formula $C_7H_{10}N_2O_2$.

It has also been obtained by the action of an aqueous solution of potassium cyanide, to which some hydrochloric acid is added, on an alcoholic solution of ethyl α-cyanopropionate.

From these facts the author concludes that the formula of the compound is $CN{\cdot}NH{:}C{\cdot}CHMe{\cdot}COOEt$. It is insoluble in cold water, and sublimes readily in a current of steam. It is easily soluble in ether and hot alcohol, slightly so in benzene and cold alcohol. The crystals belong to the rhombic system, and show a combination of the prism, brachypinacoid, and macropinacoid. A determination of the molecular weight in benzene by Raoult's method gave the theoretical number 154. M. F.

Dimethylamidopropionic Acid. By E. Duvillier (*Bull. Soc. Chim.* [3], **7**, 99—102).—*Dimethylamidopropionic acid*,

$$CH_3{\cdot}CH(NMe_2){\cdot}COOH,$$

is obtained by heating excess of an aqueous solution of dimethylamine (3 mols.) with α-bromopropionic acid (1 mol.) for several hours in a sealed tube at 100°. The product is treated with boiling barium hydrate solution, the barium carefully precipitated with sulphuric acid, and silver oxide added. The silver is removed by hydrogen sulphide and the solution warmed for 8—10 hours with freshly precipitated copper hydroxide; the copper salt thus formed is then decomposed by hydrogen sulphide, and the acid precipitated as a pasty mass by adding ether to its alcoholic solution. The syrupy aqueous solution after a time deposits the acid as slender needles; on heating, it melts and volatilises with partial decomposition. It is very soluble in water and alcohol, insoluble in ether. The *hydrochloride* crystallises in tufts of needles, and is very soluble in alcohol and water. The *platinochloride* crystallises in the monosymmetric system with 4 mols. H_2O, which are lost at 110°; it is soluble in alcohol and water, insoluble in dry ether. The *aurochloride* is obtained in monosymmetric crystals, very soluble in water, alcohol, and ether-alcohol, sparingly soluble in ether. The *stannochloride* is a deliquescent, crystalline salt, soluble in water and alcohol. The *cadmium* salt resembles the *zinc* salt, which is obtained from its aqueous solution as a syrup, but ultimately solidifies; they are both soluble in alcohol. The *copper* salt forms beautiful blue, monosymmetric crystals containing 7 mols. H_2O; the last molecule of water is only lost on prolonged heating at 120°. Aqueous solutions of the salt undergo partial reduction at 120° with deposition of metallic copper. W. J. P.

Action of Ammonia on Bromisobutyric Acid. By E. Duvillier and F. Chancel (*Bull. Soc. Chim.* [3], **7**, 102—104; compare *Bull. Soc. Chim.* [3], **5**, 848).—A mixture of bromisobutyric acid (1 mol.) and aqueous ammonia (3 mols.) was heated in a closed tube at 100° for several hours. The product was then treated with excess of barium hydroxide, the ammonia boiled off, and the barium eliminated by adding exactly the necessary quantity of sulphuric acid. On distilling the aqueous solution, a distillate was obtained from which a mixture of isobutyric acid and about 8 per cent. of a crotonic acid, probably methacrylic acid, was separated. The residual liquid from the distillation yielded hydroxyisobutyric acid on extraction with ether. By further treating the solution with silver oxide, eliminating the silver by hydrogen sulphide, evaporating to dryness, extracting with alcohol, and precipitating the alcoholic solution with ether, amidoisobutyric acid was obtained. W. J. P.

Monobromocerotic Acid. By T. Marie (*Bull. Soc. Chim.* [3], **7**, 111—113).—A *bromo*-derivative of cerotic acid, $C_{25}H_{51}{\cdot}CHBr{\cdot}COBr$, is prepared by allowing dry bromine (2·5 c.c.) to act drop by drop on an intimate mixture of cerotic acid (10 grams) and amorphous phosphorus (0·3 gram) and heating on the water-bath for six hours. The

product is poured into water and the pasty mass extracted with petroleum after washing. On repeated crystallisation from petroleum, the brominated derivative is obtained in stellate groups of needles melting at 65—66°. W. J. P.

Reciprocal Transformation of Lactones and Hydroxy-acids. By P. Henry (*Zeit. physikal. Chem.*, **10**, 96—129).—Lactones, being the internal ethereal salts of hydroxy-acids, may be hydrolysed by means of bases just like other ethereal salts; and the change in aqueous solution might be expected to obey the same laws in both cases. The author has studied the rate of hydrolysis of butyrolactone and of valerolactone by different bases in dilute solution (1/200-normal) at 25°, and finds the following velocity constants:—

Base.	Butyrolactone.	Valerolactone.	Ratio.
KOH	0·253	0·131	1·93
NaOH	0·255	0·127	2·00
$Ca(OH)_2$	0·241	0·124	1·94
$Sr(OH)_2$	0·250	0·126	1·99
$Ba(OH)_2$	0·248	0·125	1·97
NH_2Me	0·0530	0·0230	2·31
NH_2Et	0·0532	0·0268	1·98
$NHMe_2$	0·0576	0·0326	1·77
NH_3	0·02	0·01	2·00

A comparison of the numbers obtained in this way for butyrolactone with those got by Ostwald for the hydrolysis of ethyl acetate in 1/40-normal solution results as follows:—

Base.	Butyrolactone, 1/200-normal.	Ethyl acetate. 1/40-normal.
KOH	253·0	253·0
NaOH	255·0	254·0
NH_2Me	53·3	29·9
NH_2Et	53·2	29·9
$NHMe_2$	57·6	35·4
NH_3	20·0	4·7

The values for potash have been made equal in the two cases. It will be observed that the increased dilution in the case of the feebler bases greatly increases the relative velocity coefficient, owing to the increased dissociation. Calculation shows that it is the hydroxyl ion of the base that actually effects the hydrolysis.

The author also investigated the transformation of γ-hydroxybutyric and γ-hydroxyvaleric acids into their respective lactones in aqueous solution under the influence of acids. The catalytic action of the added acids is proportional to their coefficients of affinity. Hydroxyvaleric acid is more easily transformed into the lactone than hydroxybutyric acid; this corresponds with the greater stability of valerolactone as compared with butyrolactone.

The γ-hydroxy-acids do not need the addition of a foreign acid to

convert them into lactones. On standing in aqueous solution, they undergo the transformation spontaneously. This is a case of what Ostwald has called "autocatalysis," the hydrogen ions split off from the acid itself being the agents that effect the decomposition of the undissociated portion of the acid. J. W.

Stereochemistry of Trihydroxystearic Acids prepared from Ricinoleïc Acid and from Ricinelaïdic Acid. By K. Mangold (*Monatsh.*, **13**, 326—329).—A mixture of two hydroxystearic acids is formed by the oxidation of ricinoleïc acid, which, according to the investigations of Krafft, has the constitution

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH{:}CH\cdot[CH_2]_8\cdot COOH,$$

since secondary capryl alcohol and sebacic acid may be obtained from it. To account for this fact, Hazura and Grüssner (Abstr., 1888, 1270) have made the suggestion that ricinoleïc acid is not a single substance but a mixture of two acids. The author, however, points out that such a supposition is unnecessary, as a more satisfactory explanation is, that a single acid gives rise to two stereoisomeric oxidation products.

Hazura and Grüssner (Abstr., 1889, 956) obtained only one product of oxidation of ricinelaïdic acid, but the author finds that, on oxidation with alkaline potassium permanganate, two distinct acids are formed. These are well characterised; one crystallises from alcohol in microscopic prisms and from ether in microscopic rhombohedra, and melts at 117—120°; the other crystallises in slender needles and melts at 113—116°. G. T. M.

Constitution of Tiglic and Angelic Acids. By I. Kondakoff (*J. Russ. Chem. Soc.*, **22**, 375—380).—The author adduces the following observations made by him in support of the formulæ $CH_2{:}CH\cdot CHMe\cdot COOH$ and $CH_3\cdot CH{:}CMe\cdot COOH$ for angelic and tiglic acids respectively. Tiglic acid, when oxidised with potassium permanganate, yields, as products of oxidation, acetaldehyde, acetic acid, dihydroxytiglic acid, along with other neutral and acid compounds of undetermined constitution. Neither propionic nor oxalic acid is formed. The chief product is acetaldehyde. Angelic acid, on being similarly treated, yields acetaldehyde and small quantities of another aldehyde, the acid corresponding with which forms a very sparingly soluble, crystalline silver salt. Oxalic acid is formed, and another acid, which is not crystalline, is excessively hygroscopic, and whose salts are amorphous and soluble in water, but insoluble in alcohol. The calcium salt, dried at 117°, contains 16·3 per cent. of calcium.

The author also investigated the additive products obtained by the action of fuming hydriodic acid on angelic acid and its ethyl salt, and the substances produced from them by the action of moist silver oxide. J. W.

Action of Methylene Iodide on Diethyl Malonate. By S. Tanatar (*J. Russ. Chem. Soc.*, **22**, 314—317); compare Abstr., 1891, 174 and 175.—The yellow oil obtained on distilling the acid

$OEt{\cdot}CH_2{\cdot}CH(COOH)_2$ was saponified. The acid thus produced is a thick liquid which may be extracted from its aqueous solution by agitation with ether. The soluble calcium salt is precipitated by silver nitrate with formation of the salt $C_6H_8Ag_2O_5$, which blackens in the light, but remains undecomposed up to 100°; above this temperature it decomposes quietly. A strong aqueous solution of the acid heated at 160° with hydriodic acid yields yellow, shining plates (β-iodopropionic acid ?) on cooling.

The ethereal salt produced by the action of methylene iodide on ethyl malonate has the molecular weight 363, according to observations on the freezing point of its acetic acid solutions. The molecular weight of diethyl methylenemalonate is 172. On hydrolysis, it yields calcium salts of the formulæ $C_8H_6Ca_2O_9$ and $C_4H_4CaO_5$, and silver salts $C_8H_6Ag_4O_9$ and $C_4H_4Ag_2O_5$. These correspond with two gummy acids $C_4H_6O_5$ and $(C_4H_6O_5)_2 - H_2O$.

When the saponification of the oil is conducted in absence of water, another acid is formed. The potassium salt of this acid separates from its alcoholic potash solution as a viscous mass, which readily dissolves in water. The acid is soluble in water and in ether, and remains as a honey-like mass on evaporating its solutions. The lime salt has the composition and properties of calcium ethoxyisosuccinic acid. The acid heated in a sealed tube with hydriodic acid yields ethyl iodide. Its formation may be represented by the equation $CH_2{:}C(COOH)_2 + EtOH = OEt{\cdot}CH_2{\cdot}CH(COOH)_2$. J. W.

Action of Alcoholic Potash on Bromisosuccinic Acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **22**, 313—314).—If the acid $C_6H_{10}O_5$, obtained by the action of alcoholic potash on bromisosuccinic acid (Abstr., 1890, 1238), is heated with aqueous hydriodic acid, an acid melting at 140° is obtained. This acid crystallises in plates from ether, and from water in needles; its calcium salt is sparingly soluble in water. The author regards it as isomalic acid.

The acid $C_6H_{10}O_5$ would thus be ethoxyisosuccinic acid,

$$COOH{\cdot}CMe(OEt){\cdot}COOH,$$

different from the isomeric acid, $COOH{\cdot}CH(CH_2{\cdot}OEt){\cdot}COOH$, obtained from diethyl malonate by the action of methylene iodide (compare preceding abstract). No analyses are given. J. W.

Transformation of Maleïc into Fumaric Acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **22**, 310—312).—If an aqueous solution of maleïc acid (10 to 30 per cent.) is heated for two hours at 200° in a sealed tube, practically the whole of the maleïc is converted into fumaric acid. Small quantities of maleïc acid remain unchanged, and sometimes traces of a very soluble acid are found in the solution. At 160° no change takes place. If Wislicenus' explanation of the action of the halides of hydrogen in converting maleïc into fumaric acid is applied to this case, malic acid ought to be formed as an intermediate product, and should, therefore, by heating with water at 200°, be converted into fumaric acid. The author finds that this is not the case, and that the acid formed by the prolonged heating of

fumaric acid with water (*Ber.*, **14**, 2648) reproduces no fumaric acid on heating with water at 220°. Maleïc acid, heated by itself in a closed tube at 200°, is completely transformed in the course of 1—2 hours into fumaric acid.

These facts the author considers to be at variance with Wislicenus' hypothesis, and he is inclined to the assumption that atoms and atomic groups can not only move from one carbon atom to another within a molecule, but also from one corner to another of the same carbon tetrahedron. J. W.

Complete Transformation of Fumaric into Maleïc Acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **22**, 312—313).—If a mixture of equal volumes of fumaric acid and phosphoric anhydride is heated in a retort, a colourless liquid distils at 160° into the receiver, where it solidifies on cooling. This is maleïc anhydride, which may be obtained perfectly pure by recrystallisation from chloroform. On heating the anhydride with water at 50—60°, the acid is formed, and dissolves.

Fumaric acid may be distilled without decomposition under a pressure of 50—70 mm. J. W.

Tetramethylenedicarboxylic Acids. By V. Markovnikoff (*J. Russ. Chem. Soc.*, **22**, 279—290).—Markovnikoff and Krestovnikoff prepared an acid of the composition $C_6H_8O_4$ by the action of dry sodium ethoxide on ethyl α-chloropropionate. They found that this acid did not behave as an unsaturated acid, and they gave to it the name *symmetrical tetrylenedicarboxylic acid* and the formula

$$\begin{array}{l} CH_2{\cdot}CH{\cdot}COOH \\ COOH{\cdot}CH{-}CH_2 \end{array}$$

(*J. Russ. Chem. Soc.*, **11**, 455, and **12**, 460).

It crystallises from water in four-sided prisms, is easily soluble in cold absolute alcohol, but much less so in ether. 100 parts of water at 17—20° dissolve 3·8 parts of the acid. Heated for 48 hours with water containing a few drops of sulphuric acid, it remained unchanged. With hydriodic acid (sp. gr. 1·96), it showed signs of decomposition at 180°, but even after prolonged heating at 250° there was only a slight pressure of gas in the tube. No carbonic anhydride was formed, the gas evolved being combustible (C_4H_8?). The acid chloride was prepared from the sodium salt and phosphorus pentachloride at the ordinary temperature. It crystallises from ether in needles. The amide may be prepared by treating the ethereal solution of the acid chloride with strong aqueous ammonia. Silver nitrate gives no precipitate with a solution of the sodium salt at first, but after some time a crystalline powder falls out; a considerable quantity, however, remaining dissolved.

When the acid was treated with twice its weight of acetic chloride, it did not dissolve at the ordinary temperature, but did so at 90°. The solution kept over solid sodium hydroxide for a week in a vacuum left a mass of crystals melting at 166—169°; these contained chlorine

and gave off acetic chloride on heating, and are probably the acetochloranhydride, $COCl{\cdot}C_4H_6{\cdot}COOAc$. The crystals are fairly soluble in ether. The same compound is obtained, along with the mixed anhydride, by the action of acetic chloride on the silver salt. If the anhydride alone is wanted, a slight excess of the silver salt is taken, covered with a considerable quantity of ether, and acetic chloride dissolved in ether is allowed to drop slowly in. After five hours' heating with a reflux condenser, the liquid no longer contains chlorine; it is then filtered from the silver chloride, the ether distilled off, and the residue placed in a vacuum over sulphuric acid. It forms a viscous liquid heavier than water, in which it dissolves slowly in the cold, but more quickly on heating, losing at the same time its aromatic odour. The aqueous solution, on cooling, deposits the original acid, and contains acetic acid. Ethyl acetate is formed when the substance is dissolved in alcohol. A titration with soda of the aqueous solution of a weighed portion corresponded with the formula $C_4H_6(COOAc)_2$.

Heated at 150—160° in a test-tube, the mixed anhydride gives off acetic acid vapours, and tetrylenedicarboxylic acid remains. When the mixed anhydride is heated strongly in a retort, acetic anhydride distils over, the thermometer indicating a temperature of 180°. Suddenly it rises to 240°, a new substance then distilling. The distillation is stopped when the product begins to become brown. On redistillation, the higher boiling product comes over at 250—252°, solidifying in the receiver. It is the anhydride of an acid isomeric with the symmetrical dicarboxylic acid. Its melting point is 49—50°, and its boiling point 254—255° (corr.). It is moderately soluble in water, forming an acid, 33·7 parts of which dissolve at 21° in 100 parts of water. The acid crystallises in rhombs or short prisms, melts at 138—139° (uncorr.), and is very soluble in alcohol, but only very slightly in ether. It remains unchanged on being heated at 200° with weak hydrochloric acid, but a slight odour of formic acid is observable when it is heated at 250° with dilute sulphuric acid. On being heated by itself, it loses water and forms the anhydride. The sodium salt crystallises in short needles from very strong solutions. The ammonium salt is also very soluble, and crystallises in slender needles. The calcium salt is not formed by precipitation, except on heating. The barium salt, $BaC_6H_6O_4 + 2H_2O$, is precipitated when barium chloride is added to the solution of the sodium salt. Magnesium, zinc, and mercury salts are not formed by precipitation. Those of lead and copper come down in hot solution, but the precipitates dissolve again on cooling. The silver salt is a heavy, crystalline powder, very sparingly soluble in water.

The anhydride of the lower melting acid may be prepared directly from the symmetrical acid; the latter is not changed at a temperature of 300°, but on being heated rapidly with a burner, unchanged acid and the anhydride of the isomeric acid are driven over. Careful heating drives over water first, and then anhydride, which condenses in oily drops in the receiver. This oil, on being redistilled, gives the pure anhydride. The aqueous layer contains some of the corresponding acid.

Although there are many analogies between the behaviour of the

two tetrylenedicarboxylic acids and the two symmetrical diethylsuccinic acids, the author does not consider the isomerism to be of the same type in the two cases. The acid of melting point 170° he regards as paratetramethylenedicarboxylic acid, and the acid of melting point 138° as orthotetramethylenedicarboxylic acid. The latter should then be identical with Perkin's acid (m. p. 130°) from $\begin{matrix}CH_2\cdot C(COOH)_2\\ |\quad\quad |\\ CH_2\cdot C(COOH)_2\end{matrix}$. Perkin's anhydride, however, melts at 76—78° instead of 49—50°. J. W.

Specific Rotatory Power of Tartaric Acid and its Salts. By A. A. Kanonnikoff (*J. Russ. Chem. Soc.*, **22**, 369—375).—The author has shown how to calculate the specific rotatory power of a dissolved substance from observations of the minimum refraction and rotation of the plane of polarisation of two solutions of the substance having different (unknown) concentrations. The nature of the solvent has no influence on the constant, provided that it does not affect the dissolved substances chemically. For tartaric acid, the specific rotatory power, $[\alpha]_D$, is $+12\cdot46°$; for its acid salts (of sodium, lithium, potassium, ammonium), $+24\cdot48°$ on the average; and for its normal (simple or double salts) of the same metals, $+30\cdot44°$ as a mean. The salts of various organic radicles were examined in aqueous and in alcoholic solution, and in many cases the values found for them were such as to indicate a decomposition of the salt by the solvent. The following table gives the results obtained with solutions having the acid and base in proportions corresponding with the normal salts:—

Base in salt.	$[\alpha]_D$ for aqueous solution.	$[\alpha]_D$ for alcoholic solution.
Ethylamine	24·63°	30·62°
Propylamine	24·65	30·70
Isobutylamine ...	18·16	30·63
Isoamylamine ...	12·19	24·26
Diisobutylamine .	12·69	24·36
Diamylamine	12·22	18·37
Triethylamine ...	12·46	18·86
Aniline	12·62	
Orthotoluidine...	12·89	
Paratoluidine....	12·44	
Quinoline	12·36	

A comparison of these numbers with those obtained for the metallic salts shows that water decomposes to a greater or less extent the normal salts of all the bases examined. Thus the normal salts of ethylamine and propylamine are decomposed apparently into the acid salts and free base; in the case of isobutylamine, the decomposition proceeds further; and for the other bases it seems to be complete, the values obtained being practically identical with that of the free acid. Alcohol is much less active as a decomposing agent, the salts

of ethylamine, propylamine, and isobutylamine being unaffected, whilst those of the remaining bases are only partially decomposed.

J. W.

The Volatility of Carbamide and its Crystallisation by Sublimation in a Vacuum. By L. Bourgeois (*Bull. Soc. Chim.* [3], **7**, 45—47).—Wiedemann, when preparing biuret, first noticed that carbamide would volatilise without decomposition. In an open tube, sublimation occurs to a slight extent at 120—130°. If, however, the carbamide is introduced into a tube, a small plug of cotton wool placed above it, and, after exhaustion, the tube is heated in a mercury bath at 120—130° for 15 minutes, sublimation occurs rapidly, long prisms of carbamide are found entangled in the wool, and, above the plug, transparent, tetragonal and octagonal tables. Thiourea, when heated in a vacuum at 150—160°, sublimes as ammonium thiocyanate.

T. G. N.

Thiourea. By G. Carrara (*Gazzetta*, **22**, *i*, 343—347).—Hintze (*Jahresber. der Chem.*, 1884, 462) observed that in the preparation of thiourea from ammonium thiocyanate by Reynolds' method, the mother liquors (especially in presence of an excess of thiocyanate) form a deposit of silky needles; these consist of a compound of thiourea and ammonium thiocyanate in molecular proportion. The compound is best prepared by dissolving equal weights of thiourea and ammonium thiocyanate in water and allowing the solution to evaporate. The crystals melt at 144°, have a sp. gr. of 1·4307; 23·1 parts dissolve in 100 parts of water at 25°. They dissociate in aqueous solution.

The author has determined the following constants for thiourea, namely:—melting point, 169°; sp. gr. = 1·4009; solubility, 13·76 parts in 100 of water at 24°; density of aqueous solution saturated at 24° = 1·038.

S. B. A. A.

Action of Aluminium Chloride on Aromatic Hydrocarbons. By R. Heise and A. Töhl (*Annalen*, **270**, 155—171; compare Heise, Abstr., 1891, 685).—The authors have studied the behaviour of various aromatic hydrocarbons with aluminium chloride and hydrogen chloride at 100°. In the first place they confirm the conclusions arrived at by Anschütz and Immendorff (*Annalen*, **235**, 189), and find that ethylbenzene yields benzene, paradiethylbenzene, a small quantity of metadiethylbenzene, and triethylbenzene.

When isopropylbenzene is treated with aluminium chloride and hydrogen chloride at 100°, it yields propane, benzene, and meta- and para-diisopropylbenzene; the same two diisopropylbenzenes are obtained as bye-products in the preparation of isopropylbenzene by Friedel and Craft's method, so that the compounds described by Uhlhorn (Abstr., 1891, 184) as derivatives of orthodiisopropylbenzene are, in reality, the corresponding para-compounds.

Butylbenzene, treated with aluminium chloride under the conditions already mentioned, yields benzene, and meta- and para-dibutylbenzene. Orthoxylene gives, principally, metaxylene, together with small quantities of benzene, paraxylene, pseudocumene, and mesi-

tylene; paraxylene is also converted for the most part into metaxylene, the other products being the same as in the case of orthoxylene. Metaxylene yields a small quantity of benzene, paraxylene, and trimethylbenzene, but the greater portion remains unchanged. F. S. K.

Synthesis of Cymene. By L. Reuter (*Chem. Centr.*, 1892, i, 625; from *Apoth. Zeit.*, **7**, 137; compare this vol., p. 623).—By the employment of 40—50 grams of isopropyl iodide and the corresponding quantity of parabromotoluene only traces of cymene are obtained, the chief products being diisopropyl, ditolyl, stilbene, &c. If 10—15 grams of isopropyl iodide, however, are used, 3 grams of cymene (paramethylisopropylbenzene), boiling at 174—176°, can be isolated. The action is not so violent in the latter case, and the results generally are better than Brühl represents (this vol., p. 623). A. G. B.

Displacement of Hydrogen by Haloïds in Aromatic Hydrocarbons. By Miss P. Lazareff (*J. Russ. Chem. Soc.*, **22**, 385—388).—The chlorides and bromides of sodium, potassium, barium, zinc, and cadmium are all active in facilitating the introduction of bromine into the benzene molecule. 5 grams of iodine, sealed up with 50 grams of benzene and 10 of mercuric chloride, gave a colourless liquid at the end of a week in the dark. Part of the mercuric chloride was transformed into the iodide, and hydrogen chloride was evolved on the tube being opened. The authoress inclines to the opinion that the activity of salts as halogen-carriers depends in the first place on their solubility in the liquid employed. Thus mercuric chloride and bromide in the above case are more active than the corresponding salts of the alkali metals, and are also more soluble in benzene. J. W

Iodobenzenes. By Istrati and Georgescu (*Chem. Centr.*, 1892, i, 625; from *Bull. Soc. Sci. Fiz. Bucuresci*, **1**, 56; compare Abstr., 1891, 1197).—The following iodobenzenes, the last four of which have not been described heretofore (compare *Watts' Dict.*, 2nd Ed., iii), were obtained by heating benzene with iodine and strong sulphuric acid in a reflux apparatus: C_6H_5I (b. p. 185·5—186·5°); $C_6H_4I_2$ [1 : 4] (m. p. 129°; b. p. 280—282°); $C_6H_4I_2$ [1 : 2] (m. p. 7—8°; b. p. 280—282°); $C_6H_3I_3$ [1 : 2 : 4 (?)] (m. p. 85°); $C_6H_3I_3$ [1 : 2 : 3)?)] (m. p. 182—184°); $C_6H_2I_4$ [1 : 2 : 4 : 5 (?)] (m. p. 236°); $C_6H_2I_4$ (m. p. 220°). A. G. B.

Naphthenes and Polymethylenes. By V. Markovnikoff (*J. Russ. Chem. Soc.*, **22**, 275—279).—In this paper the author discusses the question of the identity of the naphthenes from Caucasus petroleum and the polymethylenes. The naphthenes proper he considers to be identical with hexamethylene (hexahydrobenzene) and its homologues. Thus, hexanaphthene is hexahydrobenzene, octonaphthene is hexahydrometaxylene, isooctonaphthene the corresponding para-compound, and nononaphthene probably hexahydropseudocumene. The naphthenes in general may also include derivatives of other polymethylene rings. Attention is drawn to the

practical identity of the boiling points of the polymethylene derivatives, and of the corresponding paraffins. J. W.

Naphthenes and their Derivatives in the General System of Organic Compounds. By V. Markovnikoff (*J. pr. Chem.* [2], **46**, 86—106).—The conclusion of the author's review of the subject (this vol., p. 1182). A. G. B.

Action of Non-metallic Nitrides and Hydronitrides on Hydroxycarbon Compounds. By R. Vidal (*Compt. rend.*, **115**, 123—124).—When phospham is heated with phenol in sealed tubes at 300°, diphenylamine is the only product, and 90 per cent. of the calculated yield is obtained.

Boron nitride, when heated with methyl alcohol in a closed vessel at about 250°, yields a distinctly crystallised borate of dimethylamine. Phenol and boron nitride at 300° yield diphenylamine. β-Naphthol under similar conditions yields a product that has the composition of dinaphthylamine, but it differs from the latter in chemical and physical properties. It melts at 225°, and does not combine with acids (compare Abstr., 1891, 1003). C. H. B.

Indothymol and Thymoquinone. By P. H. Bayrac (*Bull. Soc. Chim.* [3], **7**, 97—99).—*Indothymol*, $C_6H_2MePr<\begin{matrix}N\cdot C_6H_4\cdot NMe_2\\ |\\ O\end{matrix}$, is prepared as follows:—Nitrosodimethylaniline hydrochloride (18 grams) is dissolved in water (2 litres), heated to 35—40°, and reduced with zinc dust (15 grams). The solution of paramidodimethylaniline thus obtained is rapidly filtered into a 1 per cent. solution (1 litre) of soda containing thymol (15 grams), and potassium dichromate (10 grams) solution (500 c.c.) is then slowly added. On acidification with acetic acid, the indothymol separates, and is collected, rapidly washed with alcohol (90 per cent.), and crystallised from alcohol (95 per cent.). It forms long, anorthic, greenish needles, melting at 69·5°. It is insoluble in water, is not attacked by alkalis, gives a blue solution with alcohol, and is sparingly soluble in light petroleum, ether, and benzene, yielding violet solutions. Zinc and acetic acid reduce it, forming a leuco-base not yet isolated. Although not attacked by glacial acetic acid, indothymol is almost immediately decomposed by dilute mineral acids, with formation of derivatives of dimethylaniline and thymoquinone.

A theoretical yield of thymoquinone may be obtained by slightly heating indothymol (1 part) with 10 per cent. sulphuric acid (10 parts), and extracting the liquid with ether. The ethereal solution is evaporated, and the residue extracted with a mixture of alcohol and ether; on evaporating the liquid, pure thymoquinone separates. W. J. P.

Preparation of Carvacrol. By A. Reychler (*Bull. Soc. Chim.*, [3], **7**, 31—34).—Carvol hydrochloride (100 parts) is heated in a reflux apparatus with anhydrous zinc chloride (2 parts), and in order

to modify the violent reaction, glacial acetic acid (33 parts) is added. At 95°, hydrogen chloride begins to be evolved, and the reaction is completed at 110—120° in about 20 minutes; the major portion of the acetic acid is then distilled over, and the carvacrol separated from the remainder and from the zinc chloride by washing with water; it is then distilled, and the distillate is further purified by washing with dilute soda. The yield amounts to 90 per cent.

A solution of carvacrol in absolute alcohol does not affect the colour of ferric chloride, but the addition of a trace of water causes the solution to become green (Abstr., 1882, 1065). T. G. N.

Some Derivatives of Carvacrol. By A. Reychler (*Bull. Soc. Chim.* [3], **7**, 34—36).—Thymoquinone can be prepared by mixing solutions containing the calculated quantities of paracarvacrolsulphonic acid, obtained by the action of sulphuric acid on carvacrol, and potassium dichromate, and subsequently distilling the product of the oxidation in a current of steam. A yield of 68—70 per cent. is obtained.

Dimethylthymoquinol is prepared from thymoquinol by Nietzki's method (Abstr., 1878, 868), that is, by dissolving sodium in methyl alcohol, adding the quinol and the requisite amount of methyl iodide, and heating the mixture in a sealed tube for 12 hours. It is a yellowish oil of sp. gr. 0·998 at 22°, insoluble in water, and boils at 248—250°. It resembles the oil distilled from arnica root (this Journal, 1874, 377). T. G. N.

Asbolin. By Béhal and Desvignes (*Compt. rend.*, **114**, 1541—1544).—The asbolin of Braconnot contains small quantities of acetic and butyric acids, but consists chiefly of catechol and a homocatechol. The latter boils at 251—252°, under a pressure of 750 mm., crystallises slowly when cooled, and afterwards melts at 46°. It is very soluble in water, and is even deliquescent. It is also readily soluble in alcohol, acetic acid, or benzene, but is almost insoluble in light petroleum. When purified by crystallisation from a mixture of benzene and light petroleum, it melts at 51°. With iron salts, chloroform, and potassium hydroxide it gives the same reactions as catechol.

The only known homocatechol is usually described as a liquid. The authors find, however, that the product obtained by the action of hydrogen iodide on cresol is really a solid melting at 51°, and boiling at 251—252° under a pressure of 750 mm. It is identical in all its properties with the homocatechol from asbolin. Homocatechol precipitates gelatin from its solution, and in this respect differs from catechol. Both compounds form yellow precipitates with quinine sulphate; when crystallised from alcohol, the catechol derivative melts at 157°, and the homocatechol at 167°. It is noteworthy that the two phenols found in asbolin are the lower homologues of the two phenols occurring in creosote. C. H. B.

Acetoneresorcinol. By H. Causse (*Compt. rend.*, **115**, 49—51).—Resorcinol (50 grams) is dissolved in pure acetone (100 grams) and concentrated hydrochloric acid (50 grams) is added. After some time,

heat is developed, and an amber-coloured, oily liquid separates. This is dissolved in alcohol, heated on a water bath, and reprecipitated by the addition of water; it again separates as an oily liquid, but after some days changes to a yellowish-white solid, which can be crystallised from dilute alcohol. It forms small, anhydrous prisms, and melts at 212—213°. It is insoluble in water, benzene, chloroform, and dry ether, but dissolves in alkalis and alkali carbonates.

This product is *acetoneresorcinol*, and when dried over sulphuric acid at 30° has the composition $C_{15}H_{16}O_4$. When distilled alone, it yields acetone, resorcinol, and a carbonaceous residue, and the same products are obtained when it is distilled with zinc powder in an atmosphere of hydrogen. When precipitated from alcohol by water, it forms a hydrate, $C_{15}H_{16}O_4 + H_2O$, which separates as a white, flocculent precipitate, which gradually becomes crystalline. It also combines with ether to form red, prismatic crystals, which lose ether when exposed to air.

Acetoneresorcinol, when heated with acetic anhydride, yields a diacetate, $C_{15}H_{24}O_4Ac_2$; this separates from ether in small, white prisms which melt at 126°, and are insoluble in cold alkalis or alkali carbonates, but dissolve with hydrolysis when heated. Benzoic chloride yields a dibenzoate, $C_{15}H_{14}O_4Bz_2$, which forms small, white crystals melting at 115°. Phosphorus oxychloride yields a phosphate, $C_{15}H_{14}O_4(H_2PO_3)_2$, which, when precipitated from alcohol by water and dried, forms a yellowish-white powder; this dissolves in caustic alkalis, and is reprecipitated by acetic acid. It follows from these results that acetoneresorcinol has the constitution $CMe_2(O{\cdot}C_6H_4{\cdot}OH)_2$.

C. H. B.

Sodium Pyrogallol. By DE FORCRAND (*Compt. rend.*, **115**, 46—48). —The sodium derivatives of pyrogallol were obtained (1) by dissolving sodium in an alcoholic solution of pyrogallol, and afterwards heating at 150°; and (2) by mixing aqueous solutions of sodium hydroxide and pyrogallol, evaporating, and heating at 150°. All the operations were conducted in an atmosphere of hydrogen. The first method gives practically colourless mono-, di-, and tri-sodium derivatives, which, however, always retain a certain quantity of alcohol; the second method gives unsatisfactory results with the mono- and di-derivatives, but yields trisodium pyrogallol almost pure and colourless. Measurements of the heat developed by the action of dilute sulphuric acid, a correction being made in those cases where alcohol is retained, lead to the following results:—

$C_6H_6O_3$ sol. + Na sol. = H gas + $C_6H_5NaO_3$ sol.	develops	+ 41·34 Cal.
$C_6H_5NaO_3$ sol. + Na sol. = H gas + $C_6H_4Na_2O_3$ sol.	,,	+ 39·09 ,,
$C_6H_4Na_2O_3$ sol. + Na sol. = H gas + $C_6H_3Na_3O_3$ sol.	,,	+ 35·66 ,,
$C_6H_6O_3$ sol. + Na_3 sol. = H_3 gas + $C_6H_3Na_3O_3$	,,	+116·09 ,,

It is obvious that the value of the three phenolic functions dimin-

ishes regularly. The intermediate value is identical with that of ordinary phenol; the mean value of the first and third functions +38·5 Cal. is practically identical with the mean value in the case of resorcinol, +38·6 Cal. The mean value of the three functions, +38·70 Cal., is somewhat lower than that of phenol or the mean value for catechol, +39·02 Cal., but is greater than the mean value for resorcinol, and still greater than the mean value for quinol, +37·36 Cal.

C. H. B.

Conversion of Gallic Acid into Pyrogallol. By P. Cazeneuve (*Compt. rend.*, **114**, 1485—1487).—When gallic acid is mixed with about twice its weight of aniline, the mixture is at first liquid, but suddenly solidifies with development of heat. If the mass is heated at 120°, carbonic anhydride is evolved without any thermal disturbance, and the whole of the gallic acid can be decomposed at this temperature. As soon as evolution of gas ceases, the mixture is allowed to cool, and aniline pyrogallate separates in long needles melting at 55—56°. This salt is very unstable. In air at the ordinary temperature, or more rapidly in a vacuum, it loses aniline. When treated with benzene or toluene in the cold, aniline dissolves and pure pyrogallol is left.

Most liquid amines of the benzene series, such as orthotoluidine and the xylidines, as well as methylamine or quinoline, give similar results. Pyridine, which boils at 116·5, does not decompose gallic acid at this temperature, but when heated in sealed tubes at 130° there is progressive decomposition. The decomposition seems to be due to the intermediate formation of a gallate of the amine, less stable than gallic acid itself. Dimethylaniline, which does not combine with the gallic acid, does not decompose it even at 198°.

Pure pyrogallol melts at 132° (uncorr.), and not at 115° as usually stated. C. H. B.

Action of Phosphorus Pentachloride on Methylhydrocotoïn and Methylprotocotoïn. By P. Bartolotti (*Gazzetta*, **22**, 498—503).—Ciamician and Silber (this vol., p. 62) have prepared a substance of the composition $C_9H_9Cl_3O_3$, by the action of phosphorus pentachloride on methylprotocotoïn or methylhydrocotoïn. The author treats methylhydrocotoïn (20 grams) with phosphorus pentachloride (120 grams), and then distils off the phosphorus compounds; the distillate and residue are now treated with water, and distilled in a current of steam. A small quantity of dichlorotoluene first passes over, and then a compound of the composition $C_9H_9Cl_3O_3$; the latter, after several crystallisations from alcohol, is obtained in minute, white needles melting at 130—131°. The molecular weight, determined by the cryoscopic method, is normal.

On heating the chlorinated compound (4 grams), dissolved in absolute alcohol (200 c.c.), in a reflux apparatus, and cautiously adding excess of sodium, a solution is obtained, from which trimethylphloroglucinol may be separated by distillation in a current of steam and subsequent crystallisation from alcohol. The chlorinated compound is, therefore, trichlorotrimethylphloroglucinol, and the product

of chlorination of hydrocotoïn and protocotoïn, $C_8H_7Cl_3O_2$, should be trichlorodimethylresorcinol.

Hydrocotoïn and protocoïn must be, therefore, considered as derivatives of dimethylphloroglucinol.

Commercial hydrocotoïn (100 grams) is methylated by dissolving it in methyl alcohol (200 c.c.) containing potash (32 grams); methyl iodide (100 grams) is now added, and the solution heated on the water bath for six hours. The methyl iodide and alcohol are then distilled off, and water added to the residue; the mass after a time solidifies, and is then treated with potash to remove unaltered hydrocotoïn and protocotoïn; the crude methylhydrocotoïn thus obtained is recrystallised from alcohol. W. J. P.

Derivatives of Isoapiole. By P. Bartolotti (*Gazzetta*, **22**, 558—566).—On boiling apiole with alcoholic potash, 70 per cent. of it is converted into the isomeric isoapiole; the remaining 30 per cent. is obtained as an oil. The author now shows this to be a mixture of the two isomerides; on subsequent treatment with alcoholic potash, it is completely converted into isoapiole.

Propenyldimethylapionol, $C_3H_5{\cdot}C_6H(OMe)_2(OH)_2$ [1 : 2 : 3 : 4 : 5 or 1 : 2 : 5 : 3 : 4], is prepared by heating isoapiole (5 grams), caustic potash (10 grams), and methyl alcohol (10 c.c.), in a closed tube at 140° for eight hours; a little hydrogen is produced. The mass is dissolved in water, and the solution, after extraction with ether to remove unchanged isoapiole, is acidified with sulphuric acid, and repeatedly extracted with ether; the ethereal solution is dried, the ether distilled off, and the oily residue distilled under 50 mm. pressure; the phenol (4·5 grams) thus obtained is a yellowish, thick oil, which solidifies after a long time. The *diacetyl* derivative is prepared by boiling the phenol (27 grams) with acetic anhydride (90 grams) and anhydrous sodium acetate (15 grams) in a reflux apparatus for some time; the acetic anhydride is then distilled off, the residue treated with water, and sodium carbonate, and the crude acetyl derivative (19 grams) crystallised from alcohol and benzene. It is finally obtained in colourless crystals, which are almost insoluble in cold ether, and melt at 125—126°. It is easily hydrolysed by alcoholic alkalis.

Dimethylapionolcarboxylic acid,

$$C_6H(OH)_2(OMe)_2{\cdot}COOH\ [1 : 2 : 3 : 4 : 5 \text{ or } 2 : 3 : 1 : 4 : 5],$$

is obtained by fusing apiolic acid (5 grams) with potash (25 grams) and a little water. The fusion must be stopped when a sample dissolved in water gives no precipitate on the addition of sulphuric acid. The product of the fusion is dissolved in water, acidified with sulphuric acid, and repeatedly extracted with ether; the ether is evaporated, the residue dissolved in ethyl acetate, and after long boiling with animal charcoal the solution is allowed to crystallise, when the new acid separates in small, colourless needles melting at 147—148°. It is soluble in water, alcohol, ether, benzene, and ethyl acetate, and is precipitated as an oil by light petroleum from its solution in benzene. It gives a blue colour with

ferric chloride, turning red with sodium carbonate. With lime water, the solution of the acid gives a violet colour, and ultimately a violet precipitate. Barium hydroxide gives a blue colour, and then a green precipitate. Potassium cyanide yields a red colour. Mercuric chloride gives a black precipitate after adding ammonia. Silver nitrate solution gives no indication, but metallic silver separates on adding ammonia. Lead acetate yields a milky-white precipitate. On the addition of potash, soda, or ammonia, and exposure to air, the solution of the acid turns black. No precipitate is obtained with barium or calcium chloride, copper nitrate, or ammonium salts.

A good yield (50 per cent.) of apiolic acid is obtained by dissolving isoapiole (4 grams) in boiling water (800 c.c.) and oxidising it by the gradual addition of a boiling alkaline solution (1600 c.c.) of potassium permanganate (16 grams). W. J. P.

Organic Halogen and Boron Derivatives. By C. Chabrié (*Bull. Soc. Chim.* [3], **7**, 18—31).—Ethyl sodiomalonate and carbon tetrachloride react to form *ethyl pentaneoctocarbonate*, according to the equation $4CHNa(COOEt)_2 + CCl_4 = C[CH(COOEt)_2]_4 + 4NaCl$. This compound is a syrupy liquid, forming an amorphous potassium salt, $C[CH(COOK)_2]_4$.

On heating sodium phenoxide with carbon tetrachloride in sealed tubes at 125°, aurine is formed, probably by the elimination of hydrogen chloride from the compound $CCl(C_6H_4{\cdot}OH)_3$, previously produced.

In addition to the fluorine derivatives previously described (Abstr., 1890, 558, 1053; 1891, 353), the author has prepared fluoroform by heating chloroform with silver fluoride. It is a colourless gas of characteristic odour, very slightly soluble in aqueous, but soluble in alcoholic potassium hydroxide, yielding potassium formate. The results of experiments on the antiseptic values of these fluorine derivatives are given.

On heating amorphous boron with the chlorides of carbon, with ethylene dibromide, and with tribromhydrin, the author found that in each case a replacement of carbon by boron occurred.

T. G. N.

Constitution of the Dihydroxythiobenzenes. By G. Tassinari (*Gazzetta*, **22**, 504—507).—The author has tried to prepare paranitrophenyl sulphide, $(NO_2{\cdot}C_6H_4)_2S$, by the action of paranitrothiophenol on salts of diazoparanitrobenzene under different conditions. The only product of the reaction which could be isolated was a small quantity of paranitrophenyl bisulphide. Analogous results were obtained with diazometanitrobenzene. On diazotising paraphenetidine, and adding hydrogen sulphide, yellow flocks separated; these decomposed very slowly at ordinary temperatures, but on heating for a few hours they yielded nitrogen and a resin. The precipitate, on extraction with alcohol, gave a small quantity of a substance which seemed to be "dioxythiophenetoïl" (ethoxyphenyl sulphide), $S(C_6H_4{\cdot}OEt)_2$,

melting at 51—58°, prepared from the dihydroxythiobenzene melting at 150—151°.

Parabromaniline, when diazotised and treated with hydrogen sulphide, yields a resin which, on extraction with alcohol, gives a fair yield of a crystalline compound. This substance, on crystallisation from carbon bisulphide, yields a very small quantity of red needles melting at 205—206°, probably consisting of a nitro-compound, and a crop of pearly-white scales, which melt at 112—113°. The latter substance is identical with the bromophenyl sulphide obtained from thioaniline or by brominating phenyl sulphide. This bromophenyl sulphide should be a dipara-derivative; hence the dihydroxythiobenzene, prepared by the action of sulphur chloride on phenol, is also a dipara-derivative. W. J. P.

Thiopinacone. By W. Spring and J. van Marsenille (*Bull. Soc. Chim.* [3], **7**, 13—16).—When cinnamene dibromide is heated with an alcoholic solution of potassium hydrogen sulphide in sealed tubes at 120—130° for 30 hours, the contents separate into two layers, one of which is an uncrystallisable yellowish, oily liquid, of penetrating odour. This is free from bromine, and evolves hydrogen sulphide when warmed under reduced pressure. It could not be purified sufficiently for analysis, but on treating it with warm potassium hydroxide until potassium sulphide was no longer formed, a thiopinacoline, C_8H_8S, was obtained, probably by the separation of a molecule of hydrogen sulphide from the phenylthioglycol, $CHPh(SH)\cdot CH_2\cdot SH$, first formed. This thiopinacone is insoluble in water, slightly soluble in alcohol, and is soluble in a mixture of alcohol and ether, in light petroleum, in carbon bisulphide, and in benzene. Its sp. gr. at 16° is 1·0988, and on oxidation with chromic anhydride it yields benzoic acid, behaving in this respect like the pinacone, C_8H_8O (this Journal, 1877, ii, 614), but it differs from the isomeric xylylene sulphide (Abstr., 1884, 1313), which is crystalline, and can be distilled in a current of steam. T. G. N.

Carbaminethioacetophenone. By G. Marchesini (*Gazzetta*, **22**, i, 350—354).—Arapides (Abstr., 1889, 413) prepared carbaminethioacetophenone hydrochloride by prolonged heating of acetophenone thiocyanate with concentrated hydrochloric acid, but was unable to isolate the base, on account of its alleged instability. On mixing an aqueous solution of freshly prepared ammonium thiocarbamate with a saturated alcoholic solution of bromacetophenone in molecular proportion, and keeping the mixture cool, a white powder is precipitated, which, after drying in a vacuum, has the composition

$$COPh\cdot CH_2\cdot S\cdot CONH_2.$$

It melts at 120°, but subsequently solidifies, melting again at 204°. It dissolves in alcohol, but on heating and evaporating the solution, phenylhydroxythiazole (m. p. 204°) crystallises out. The *phenylhydrazine* derivative, $CPh(N_2HPh)\cdot CH_2\cdot S\cdot CONH_2$, prepared by agitating a mixture of carbaminethioacetophenone and phenylhydrazine,

in molecular proportion at the ordinary temperature, crystallises, when pure, in yellowish needles, melts at 130°, and dissolves in alcohol, ether, and chloroform. If a mixture of ammonium thiocarbamate and bromacetophenone is heated in a reflux apparatus in presence of alcohol, the principal product is phenylhydroxythiazole, whilst ammonium bromide and phenacyl sulphide are formed as intermediary products.

An aqueous solution of ammonium thiocarbamate gives the following reactions:—With lead salts, a brownish precipitate, changing to black, which evolves carbonic anhydride on treatment with cold nitric acid, and also hydrogen sulphide, on warming; with an excess of manganous sulphate, no precipitate is obtained in the cold, but on warming, a flesh-coloured precipitate, soluble in dilute nitric acid, is formed; on warming with barium chloride, a white precipitate, soluble with effervesence in dilute acids, is produced; with nickel sulphate, a black precipitate is obtained, resembling nickel sulphide, and soluble in dilute nitric acid; with copper sulphate, a brown precipitate, which blackens on heating, and dissolves in dilute nitric acid; with an excess of mercuric chloride, a dirty-white precipitate of the mercurous salt, $HgS{\cdot}CONH_2$, is formed; this rapidly darkens in the air, and dissolves in dilute hydrochloric or nitric acid. S. B. A. A.

Reduction of Coumarone. By H. Alexander (*Ber.*, **25**, 2409—2411).—*Hydrocoumarone*, C_8H_8O, is obtained by adding a boiling solution of coumarone in five times the quantity of absolute alcohol to sodium contained in a reflux apparatus, and then adding boiling alcohol until all the sodium is converted into sodium ethoxide. The product is mixed with water and the alcohol distilled off, when an oil passes over along with the alcohol, and can be precipitated by adding water to the distillate. The aqueous solution also contains some of the oil, which is separated by steam distillation. The oil is dissolved in ether, the ethereal solution washed with soda and then with water, and the ether evaporated. The residue is freed from coumarone by treatment with sulphuric acid, and finally the oil is dissolved in ether, dried, and fractionally distilled. It boils at 188—189°, is colourless, has a pleasant odour, and is soluble in ether, alcohol, chloroform, and carbon bisulphide, but insoluble in water. It is volatile with alcohol vapour, more easily with steam, is soluble in alkalis, and is not resinified by concentrated sulphuric acid. The sp. gr. at 23° = 1·06488. With ferric chloride and concentrated sulphuric acid, it gives a violet coloration.

On adding sulphuric acid to the aqueous liquid from which the hydrocoumarone has been separated, orthoethylphenol separates as an oil, which can be purified by steam distillation. It boils at 202—203° (uncorr.), turns yellow on exposure to the air, is easily soluble in alcohol, ether, and alkalis, and is very hygroscopic. With ferric chloride, it gives a greenish-grey coloration, and, when melted with potash, yields salicylic acid.

Orthoethylphenol is described as boiling at 206—207° (*Annalen*, **102**, 166; *Ber.*, **17**, 670). E. C. R.

Fluorescin, Galleïn, and Aurin. By J. Herzig (*Monatsh.*, **13**, 422—428).—The formation of colourless acetyl derivatives from quercetin, ethylquercetin, &c. (see Abstr., 1891, 1349), renders it possible that these are not derivatives of the original colouring matter, but of the corresponding leuco-derivative. Owing to the high molecular weights of these substances, the elementary analysis is insufficient to decide whether this is really the case, and the author has therefore examined the behaviour towards acetic anhydride of analogous compounds of lower molecular weight. Such a group is found in Baeyer's phthaleïns.

The melting points of acetylphenolphthaleïn and acetylphenolphthalin, on the one hand, and of acetylfluoresceïn and acetylfluorescin, on the other, are almost identical, and it appeared possible, therefore, that in the acetylation of fluoresceïn reduction might simultaneously take place, in which case the resulting compound would be identical with acetylfluorescin. On further investigation, this view was, however, found to be incorrect, the compounds, although similar in many respects, behaving quite differently towards alkalis.

Fluorescin was described by Baeyer as an oil, but may be obtained crystalline by triturating the syrup with acetic acid; it forms white needles melting at 125—127°, and becomes yellow in the air, when it has a melting point varying between 125° and 130°. On acetylation, it yields acetylfluorescin, which closely resembles acetylfluoresceïn in appearance, and melts at 200—202°. When treated with dilute alkali, however, it only dissolves in so far as it is hydrolysed, whilst acetylfluoresceïn dissolves readily, and, if the solution is quickly acidified, separates again unaltered.

The ethyl ethers of phenolphthalin and of fluorescin are readily obtained by saturating their alcoholic solutions with hydrogen chloride; the former crystallises from dilute alcohol in long needles which melt at 150—152° (uncorr.), and the latter from acetic acid in needles melting at 195—196°, and becoming yellow on exposure to air.

The acetyl derivatives of galleïn have already been examined by Buchka (*Annalen*, **209**, 261; Abstr., 1882, 59), who, by the reduction of galleïn, obtained, in addition to gallin, an intermediate hydrogalleïn. The author, in repeating these experiments on a smaller scale, was unable to obtain the latter compound, and found that acetylgalleïn and acetylgallin melt at 234—237° and 211—213° respectively, instead of 247—248° and 220°, as given by Buchka.

Results have also been obtained with acetylaurin and acetylrosolic acid, which are not in accordance with previous statements; further investigations on this point are in progress. H. G. C.

Influence of Nucleal Methyl on the Properties of Orthotoluidine. By A. Rosenstiehl (*Compt. rend.*, **115**, 180—182).—Weinberg's observations that the alkyl and amidated alkyl derivatives of orthotoluidine behave quite differently from the corresponding derivatives of aniline (this vol., p. 1078) may be explained by supposing that the former are virtually desmotropic, the methyl group wandering from the ortho-position either to the amido-group, or,

where this is fully substituted, to the position para- to the amido-group. Jn. W.

Action of Formaldehyde on Orthodimethyltoluidine. By H. Alexander (*Ber.*, **25**, 2408).—A base of the composition

$$NMe_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot C_6H_4 \cdot NMe_2,$$

is formed on heating orthodimethyltoluidine (9 grams) with solid formaldehyde (2 grams) and aqueous zinc chloride (0·5 per cent., 6 grams) for 18 hours at 170—180°. The product is distilled with steam, when the above base remains unvolatilised, any unaltered dimethyltoluidine being separated. It yields a sparingly soluble *platinochloride*, which melts above 200° with decomposition. The *base*, obtained by decomposing the platinochloride, distils as a colourless oil at 227—229° under a pressure of 40 mm., and is insoluble in water, but easily soluble in alcohol, ether, and chloroform. It has very feeble basic properties, and, with concentrated hydrochloric acid, yields a *hydrochloride*, which crystallises in beautiful, silky needles and easily decomposes with evolution of hydrogen chloride.

E. C. R.

Action of Benzyl Chloride on Unsymmetrical Metaxylidine. By Jablin-Gonnet (*Bull. Soc. Chim.* [3], **67**, 50—53).—*Methylbenzylmetaxylidine*, $C_6H_3Me_2 \cdot NMe \cdot C_7H_7$, is prepared by heating benzylmetaxylidine (3 mols.) and methyl iodide (2 mols.) in a reflux apparatus for 50 hours, neutralising the product with dilute sodium carbonate solution, extracting the supernatant, dark-brown liquid with benzene, and subsequently distilling it under reduced pressure. It is a yellowish liquid, insoluble in the ordinary solvents, and distils at 205—210°.

Acetylbenzylmetaxylidine, $C_6H_3Me_2 \cdot NAc \cdot C_7H_7$, is obtained similarly by the action of benzylmetaxylidine (2 mols.) on acetic chloride (1 mol.). It distils under a pressure of 10 mm. at 215—220° as a colourless liquid, rapidly turning yellow on exposure to air.

The ethyl derivative is prepared in like manner, and distils at 230—235°, but is less stable, and resinifies on exposure to air.

Benzoylbenzylmetaxylidine, $C_6H_3Me_2 \cdot NBz \cdot C_7H_7$, is formed on heating benzoic chloride (2 mols.) with benzylmetaxylidine (3 mols.) until hydrogen chloride is no longer evolved. After treatment with sodium carbonate and extraction with benzene, it distils under a pressure of 10 mm. at 240—245° as a greasy, straw-coloured liquid, which dissolves in benzene, ether, and alcohol; it is deposited from its solutions in white, prismatic crystals, melting at 85—86°.

Nitrobenzylmetaxylidine, $NO_2 \cdot C_6H_2Me_2 \cdot NH \cdot C_7H_7$, obtained by acting on benzylmetaxylidine with a mixture of sulphuric and nitric acids, is an orange-coloured substance, which is soluble in benzene, alcohol, and ether.

Benzylmetaxylidinesulphonic acid, $SO_3H \cdot C_6H_2Me_2 \cdot NH \cdot C_7H_7$, is obtained by the action on benzylmetaxylidine on sulphuric acid containing 10 per cent. sulphuric anhydride at 140—150°. It crystallises in prisms, and on oxidation is turned blue. T. G. N.

Action of Arsenious Chloride on Tertiary Aromatic Amines. By A. Michaelis and J. Rabinerson (*Annalen*, **270**, 139—147; compare Michaelis and Schenk, Abstr., 1891, 435).—*Dimethylamidophenylarsine oxide*, $NMe_2 \cdot C_6H_4 \cdot AsO$, is formed, together with hexamethyltriamidotriphenylarsine, when dimethylaniline (15 grams) is warmed with arsenious chloride (25 grams), and the mixture then treated with excess of concentrated soda; the filtered solution of the dimethylamidophenylarsine oxide is acidified with hydrochloric acid, and the base precipitated with sodium carbonate; it is a colourless powder, melts at 75°, and dissolves freely in chloroform and hot alcohol, but is insoluble in water. The *hydrochloride*, $C_8H_{10}N \cdot AsCl_2,HCl$, crystallises in slender, colourless needles, melts at 116°, and is readily soluble in water, but only sparingly in concentrated hydrochloric acid. The *hydrobromide* and the *hydriodide* were also prepared.

Dimethylamidophenylarsine sulphide, $NMe_2 \cdot C_6H_4 \cdot AsS$, prepared by passing hydrogen sulphide into an alcoholic solution of the corresponding oxide, crystallises from chloroform in colourless needles, melts at 187°, and is decomposed by hot hydrochloric acid with evolution of hydrogen sulphide.

Tetramethyldiamidoarsenobenzene, $NMe_2 \cdot C_6H_4 \cdot As:As \cdot C_6H_4 \cdot NMe_2$, can be obtained by reducing dimethylamidophenylarsine oxide with sodium amalgam in alcoholic solution; it separates from a mixture of alcohol and chloroform in the form of a yellow, semi-crystalline powder, melts at 202°, and is insoluble in water and alcohol, but readily soluble in chloroform and dilute acids. The *hydrochloride* is a red, crystalline compound, and, like the base, readily oxidises on exposure to the air.

Hexamethyltriamidotriphenylarsine, $As(C_6H_4 \cdot NMe_2)_3$, prepared by treating dimethylaniline with arsenious chloride at the ordinary temperature, crystallises from hot alcohol in long, colourless needles, melts at 240°, and is very readily soluble in chloroform, but only sparingly in cold alcohol.

Diethylamidophenylarsine oxide, $NEt_2 \cdot C_6H_4 \cdot AsO$, is a light yellow powder, melts at 58°, and dissolves freely in hot alcohol and in dilute mineral acids. The *dichloride*, $NEt_2 \cdot C_6H_4 \cdot AsCl_2$, crystallises in colourless needles, melts at 139°, and is very readily soluble in water, but only sparingly in concentrated hydrochloric acid. The *sulphide*, $NEt_2 \cdot C_6H_4 \cdot AsS$, forms colourless needles, melts at 155°, and dissolves freely in chloroform, but is insoluble in alcohol.

Tetrethyldiamidoarsenobenzene, $NEt_2 \cdot C_6H_4 \cdot As:As \cdot C_6H_4 \cdot NEt_2$, is a semi-crystalline, yellow powder melting at 180°; it is readily soluble in chloroform, but insoluble in alcohol. F. S. K.

Constitution of Nitrosoazo-Compounds. By C. Willgerodt (*J. pr. Chem.* [2], **46**, 128—141).—The author describes his most recent method for preparing dinitrosoazobenzene; it differs from that of Kehrmann and Messinger (this vol., p. 889) by the substitution of sodium hydrogen carbonate (1 mol.) for sodium acetate. The base obtained by the reduction of dinitrosoazobenzene (*loc. cit.*) is best isolated from the stannochloride by treating it with sodium hydroxide and recrystallising the precipitate from alcohol. This

base gives fluorescesent solutions in most alcohols, and in several other liquids besides those mentioned by Kehrmann and Messinger (*loc. cit.*). Analyses of the base indicate the formula $PhN_3{:}C_6H_3{\cdot}NH_2$, which is confirmed by analysis of the *platinochloride*,

$$(C_{12}H_{10}N_4)_2,H_2PtCl_6,$$

and the conclusion is inevitable that it is amidophenylazimidobenzene. At the same time, the author does not admit that Kehrmann and Messinger are right in inferring from this, that dinitrosoazobenzene is nitrophenylazimidobenzene (*loc. cit.*) ; for he regards the reduction as consisting of a preliminary conversion of the azo-group in the dinitrosoazobenzene into a hydrazine group, followed by the elimination, as water, of the two hydrogen atoms thereof, together with the oxygen of one of the nitroso-groups, leaving an azimido-group.

The reduction of nitronitrosoazobenzene (5 grams) by heating it with stannous chloride (22 grams) in fuming hydrochloric acid (46 grams) and alcohol (200 c.c.) yields a base which crystallises in somewhat shorter and broader needles than those of amidophenylazimidobenzene, and melts at 183° (uncorr.); its solutions also fluoresce, but rather more strongly than those of amidophenylazimidobenzene. This base is being further examined.

Amidoparatolylazimidobenzene, $NH_2{\cdot}C_6H_3{<}\overset{N}{\underset{N}{|}}{>}N{\cdot}C_6H_4Me$, is formed when paratolyldinitrosoazobenzene (8 grams) is heated with stannous chloride (25·2 grams) in strong hydrochloric acid (50 grams) and alcohol (250 c.c.) for 20—25 minutes in a reflux apparatus, the stannochloride being afterwards decomposed by sodium hydroxide. It crystallises in pale-green, silky needles, melts at 212—213° (uncorr.), and dissolves sparingly in alcohol with a greenish-blue fluorescence ; its solutions in ether, benzene, and chloroform also fluoresce, but those in glacial acetic acid and carbon bisulphide do not. The *platinochloride*, $(C_{13}H_{12}N_4)_2,H_2PtCl_6$, was prepared. By acting on the base with reducing agents, a compound melting at 118°, and apparently identical with tolylazimidobenzene was obtained.

A controversial appendix has reference to Kehrmann's latest remarks (this vol., p. 1198). A. G. B.

Oxidation of Phenylhydrazine with Fehling's Solution. By H. Strache and M. Kitt (*Monatsh.*, **13**, 316—319).—E. Fischer has shown (*Annalen*, **190**, 101) that phenylhydrazine is oxidised by cold Fehling's solution with formation of benzene and aniline, whilst Strache has pointed out (this vol., p. 546) that when hot Fehling's solution is employed, the whole of the nitrogen evolved in the elementary state. In order to determine the quantity of alkaline cupric oxide required to bring about the oxidation in the latter case, the authors have allowed a solution of phenylhydrazine hydrochloride to run into a known volume of boiling Fehling's solution, until complete decolorisation ensued. The experiments showed that, for every molecule of phenylhydrazine employed, 3 mols. of cupric oxide were reduced to cuprous oxide, and

that neither aniline nor any other compound containing nitrogen was evolved, benzene and phenol being the other products of oxidation.

G. T. M.

Action of Cyanogen Chloride on Phenylhydrazine. By G. Pelizzari and D. Tivoli (*Gazzetta*, **22**, i, 226—236).—*Anilcyanamide*, $NHPh\cdot NH\cdot CN$, prepared by passing a current of cyanogen chloride through an ethereal solution of phenylhydrazine, is a red, oily compound very soluble in ether, alcohol, and benzene, but insoluble in water. It becomes altered on standing, and polymerises when slightly warmed. The *picrate*, $NHPh\cdot NH\cdot CN,C_6H_2(NO_2)_3\cdot OH$, crystallises from alcohol in slender needles, melts with decomposition at 198°, and dissolves readily in hot alcohol and benzene, but only very sparingly in ether and water. The *hydrochloride* is a white powder probably containing 2 mols. HCl when freshly prepared, but slowly losing hydrogen chloride on drying in a vacuum; it is freely soluble in alcohol, but insoluble in ether and benzene. It does not form a platinochloride or aurochloride, the metallic salts being reduced. It readily dissolves in water, but is at once converted into phenylsemicarbazide, which separates from the solution. When a well-cooled alcoholic solution of the hydrochloride is treated with ammonium hydrosulphide, an orange-yellow solution is formed, from which yellowish crystals of phenylsemithiocarbazide are deposited after a time.

Dianildicyandiamide is obtained by evaporating the ethereal solution of anilcyanamide to dryness on the water-bath. It separates from alcohol in pale rose-coloured, transparent, triclinic crystals, $a : b : c = 0{\cdot}9215 : 1 : 0{\cdot}5556$. The crystals contain 1 mol. of alcohol of crystallisation, which they lose at 100°, becoming dull and opaque. It melts with decomposition at 185°, and dissolves freely in hot alcohol, but is insoluble in ether. It readily dissolves in dilute acids, and is reprecipitated unchanged on the addition of potash. The *hydrochloride* $(PhN_2H_2CN)_2,HCl$, forms small, white crystals melting at 222°, readily soluble in water or alcohol. The *picrate*,

$$(PhN_2H_2CN)_2\cdot C_6H_3O(NO_2)_3,$$

crystallises from alcohol in lemon-yellow needles melting at 184°; it is very soluble in alcohol and moderately so in hot water. When heated on platinum foil, it melts and decomposes with violence. The constitution of dianildicyandiamide is probably

$$\begin{array}{l} NHPh\cdot N\text{—}C{:}NH \\ \quad\quad\ |\quad\quad\ | \\ \quad\quad CN\quad NH\cdot NHPh \end{array}$$

S. B. A. A.

Action of Phenylhydrazine on Carbamide. By L. Edeleanu (*Chem. Centr.*, 1892, i, 628).—*Phenylsemicarbazide*, $NH_2\cdot CO\cdot N_2H_2Ph$, is formed when phenylhydrazine is heated with carbamide; it crystallises in colourless laminæ, and melts at 172°. Another colourless substance, melting at 148—149°, and somewhat more soluble in alcohol, is obtained at the same time. A solution of phenylsemicarbazide gives a violet colour with mercuric chloride, and, after a time, a violet precipitate separates, which dyes silk violet; the colour is fast in water, and intensified by soap. Acids partially dissolve this

precipitate, yielding colourless solutions, from which the colouring matter is reprecipitated by alkali carbonates; concentrated alkalis, however, decompose it. If the mercury is removed from the filtrate from the mercuric chloride precipitate by means of hydrogen sulphide, a cherry-red liquid is obtained which, on evaporation, leaves a violet-black basic substance, soluble in alcohol with a violet colour and in strong sulphuric acid with a blue colour. With copper sulphate, phenylsemicarbazide solution gives a blue precipitate which behaves similarly to the mercury precipitate. The substance which melts at 148—149° also gives colouring matters with mercuric chloride and copper sulphate. A. G. B.

Inorganic Derivatives of Phenylhydrazine. By A. Michaelis (*Annalen*, **270**, 108—113).—General remarks on the papers by the author and Ruhl and the author and Oster (compare following abstracts). The results of the experiments here discussed, and of those previously published (Abstr., 1890, 617), go to show that sulphurous acid is an aldehyde acid of the constitution $H\cdot SO_2\cdot OH$; from the behaviour of the phosphorus compounds, it is probable that phosphorous acid has the constitution $H\cdot PO(OH)_2$, and phosphenous acid the constitution $H\cdot PO(OH)\cdot Ph$. F. S. K.

Thionyl Chloride and Aromatic Hydrazines. By A. Michaelis and J. Ruhl (*Annalen*, **270**, 114—122; compare Abstr., 1890, 617).—Thionylparatolylhydrazone crystallises in long, yellow needles, and melts at 112°.

Thionyl-α-naphthylhydrazone, $C_{10}H_7\cdot NH\cdot N{:}SO$, prepared by treating α naphthylhydrazine with thionyl chloride in ethereal solution, crystallises from hot alcohol in yellowish-red plates, and melts at 100°. The corresponding β-compound crystallises from hot alcohol in yellowish-red plates, and melts at 136—139° with decomposition.

Thionylmethylphenylhydrazone, $NMePh\cdot N{:}SO$, is formed when thionylaniline (Abstr., 1891, 715) is treated with methylphenylhydrazine in acetic acid solution; it crystallises from hot alcohol in small, yellow needles, melts at 77°, and is readily decomposed by alkalis, yielding methylphenylhydrazine and a sulphite.

Thionylisobutylphenylhydrazone, $C_4H_9\cdot NPh\cdot N{:}SO$, prepared in like manner, is a yellow liquid having a peculiar penetrating odour.

Thionylbenzylphenylhydrazone, $C_7H_7\cdot NPh\cdot N{:}SO$, crystallises from hot light petroleum in yellow prisms, and melts at 65°.

Thionylethylenephenylhydrazone, $C_2H_4(NPh\cdot N{:}SO)_2$, prepared by treating ethylenephenylhydrazine with thionyl chloride or with thionylaniline, crystallises from hot alcohol in lustrous, yellow plates melting at 121—123°. F. S. K.

Action of the Chlorides of Phosphorus, Arsenic, Boron, and Silicon on Aromatic Hydrazines. By A. Michaelis and F. Oster (*Annalen*, **270**, 123—139).—When phenylhydrazine is treated with phosphorus trichloride in well-cooled ethereal solution, a semi-solid compound is formed free from chlorine, and which has, in all probability, the constitution $NHPh\cdot NH\cdot P{:}N\cdot NHPh$; when this

substance is treated with water, it is gradually converted into a yellowish, seemingly amorphous powder, which is the *dihydrazide* of phosphorous acid, $OH{\cdot}P(N_2H_2Ph)_2$. The last-named compound sinters and partially decomposes at 80°, and is readily soluble in chloroform, ethyl acetate, and alcohol, but insoluble in benzene, ether, and light petroleum; it is only very slowly decomposed by boiling alkalis, but readily by acids, and it reduces Fehling's solution in the cold; when treated with benzaldehyde, it is decomposed with formation of benzylidenephenylhydrazone, and, on oxidation with yellow mercuric oxide in chloroform solution, it is converted into a red, vitreous substance which melts at 94—95°.

Phosphenylphenylhydrazine, $PPh{:}N{\cdot}NHPh$, prepared by treating phenylhydrazine with phosphenyl chloride in well-cooled ethereal solution, crystallises from ethyl acetate in small plates, melts at 152°, and is readily soluble in chloroform, but only sparingly in cold ethyl acetate, ether, and alcohol. It reduces Fehling's solution on warming, and is readily decomposed by acids, but is more stable towards boiling alkalis; when boiled with water, it is gradually converted into phenylhydrazine phosphenite (see below).

Phosphenylparatolylhydrazone, $PPh{:}N{\cdot}NH{\cdot}C_6H_4Me$, crystallises in small, colourless or yellowish prisms, melts at 162°, and is converted into tolylhydrazine phosphenite by boiling water.

Phosphenylbenzylphenylhydrazone, $PPh{:}N{\cdot}NPh{\cdot}C_7H_7$, crystallises from a mixture of ether and chloroform in colourless needles, melts at 141°, and is readily soluble in alcohol, ethylacetate, and chloroform, but more sparingly in ether, and insoluble in water; it reduces Fehling's solution on boiling, and is decomposed into its components by acids, but is very stable towards boiling alkalis; on prolonged boiling with water, it is converted into benzylphenylhydrazine phosphenite.

Phenylhydrazine phosphite, $(N_2H_3Ph)_2,H_3PO_3$, crystallises in nacreous plates, melts at 121°, and is readily soluble in water and alcohol. The *acid salt*, N_2H_3Ph,H_3PO_3, forms large plates, melts at 118°, and dissolves freely in alcohol and water.

Phenylhydrazine phosphenite, N_2H_3Ph,PH_2PhO_2, crystallises in long, colourless prisms, melts at 135°, and is readily soluble in alcohol and boiling water, but only very sparingly in cold water. The *paratolylhydrazine* salt, $N_2H_3{\cdot}C_6H_4Me,PH_2PhO_2$, crystallises in slender, colourless needles, melts at 148°, and is readily soluble in alcohol and hot water, but only sparingly in cold water.

Phenylhydrazine paratolylphosphenite, $N_2H_3Ph,PH_2O_2{\cdot}C_6H_4Me$, prepared from its components, melts at 161°, crystallises in slender needles, and is readily soluble in hot alcohol, but only sparingly in boiling water.

Benzylphenylhydrazine phosphenite, $N_2H_2Ph{\cdot}C_7H_7,PH_2PhO_2$, crystallises in long, colourless prisms, and melts at 108°.

Phosphorylphenylhydrazide, $PO(N_2H_2Ph)_3$, prepared by treating phosphorus oxychloride with phenylhydrazine in well-cooled ethereal solution, crystallises from hot alcohol in small, colourless needles, melts at 196°, and turns brown on exposure to the air; it dissolves freely in alcohol and ethyl acetate, but is insoluble in chloroform,

ether, and benzene; it reduces Fehling's solution on warming, and is readily decomposed by alkalis and acids.

Phosphoryltolylhydrazide, $PO(N_2H_2\cdot C_6H_4Me)_3$, crystallises in slender, colourless needles, melts at 189°, and quickly turns yellow on exposure to the air.

Thiophosphorylphenylhydrazide, $PS(N_2H_2Ph)_3$, separates from ethyl acetate in slender, colourless needles, melts at 154°, and is readily soluble in alcohol, but insoluble in chloroform, ether, and benzene; when heated with water, it is slowly converted into phosphorylphenylhydrazide with evolution of hydrogen sulphide.

A compound of the composition $AsCl_3.3N_2H_3Ph$ is formed when phenylhydrazine is treated with arsenic trichloride in ethereal solution; it is a colourless, amorphous powder, turns black at 190°, decomposes completely at 236°, and dissolves in water with decomposition.

Boron trichloride and phenylhydrazine combine under the same conditions to form a compound of the composition $BCl_3,3N_2H_3Ph$; this substance decomposes completely at 242°, and is readily soluble in water, but insoluble in chloroform and ethyl acetate.

Silicon tetrachloride and phenylhydrazine combine to form a yellow, crystalline, unstable substance which is free from chlorine.

F. S. K.

Parathiophenylhydrazine and Thionylthioaniline. By J. Ruhl (*Annalen*, **270**, 148—154; compare Abstr., 1891, 301).—*Thionylthioaniline*, $S(C_6H_4\cdot N{:}SO)_2$, prepared by treating thioaniline with thionyl chloride in benzene solution, crystallises in reddish-yellow prisms, melts at 110°, and decomposes on exposure to the air.

Parathiophenylhydrazine (*loc. cit.*) melts at 114°, and is only sparingly soluble in cold chloroform and cold benzene; its hydrochloride crystallises in small prisms, and melts at 208—209° with decomposition; its sulphate melts at 219° with decomposition, and crystallises from hot dilute sulphuric acid in prisms. The *oxalate*, $S(C_6H_4\cdot N_2H_3)_2,C_2H_2O_4$, is a crystalline powder. The *acetyl* derivative, $S(C_6H_4\cdot N_2H_2Ac)_2$, crystallises from hot chloroform in small, colourless needles, and melts at 170—171° with decomposition.

Benzylidenethiophenylhydrazone, $S(C_6H_4\cdot NH\cdot N{:}CHPh)_2$, separates from alcohol in crystals, and melts at 185°.

Acetophenonethiophenylhydrazone, $S(C_6H_4\cdot NH\cdot N{:}CMePh)_2$, is a colourless crystalline powder, and melts at 170° with decomposition.

Pyruvic acid thiophenylhydrazone, $S(C_6H_4\cdot NH\cdot N{:}CMe\cdot COOH)_2$, is a yellow, amorphous substance.

Tetraphenylthiodithiosemicarbazide, $S(C_6H_4\cdot N_2H_2\cdot CS\cdot NHPh)_2$, prepared by treating thiophenylhydrazine with phenylthiocarbimide in alcoholic solution, crystallises from hot alcohol in slender needles, and melts at 180—182° with decomposition.

Thionylthiophenylhydrazone, $S(C_6H_4\cdot NH\cdot N{:}SO)_2$, is a yellow, crystalline powder, melts at 187°, and is only sparingly soluble in hot alcohol.

F. S. K.

Imidazoles and the Constitution of Glyoxaline. By W. Marckwald (*Ber.*, **25**, 2354—2373).—The author has shown that when phenyl- and methyl-acetalylthiocarbamide are treated with acid, alcohol

is eliminated, and mercaptans of the imidazole series are formed, according to the equation $CS<^{NHR}_{NH\cdot CH_2\cdot CH(OEt)_2} = \begin{matrix} HS\cdot C\cdot NR\cdot CH \\ \| \quad\quad | \\ N\text{——}CH \end{matrix}$ + 2EtHO. When these are oxidised, hydrogen is substituted for the hydrosulphide group, with formation of sulphuric acid and ν-phenyl- and ν-methylimidazole are obtained. The latter is identical with methylglyoxaline. This reaction confirms Japp's formula for glyoxaline.

The author has prepared glyoxaline synthetically by this method, and also a number of substitution products of imidazole analogous to ν-phenylimidazole.

Amidoacetal, from which the compounds described below are obtained, is best prepared by employing a large excess of ammonia, namely, 20 parts of saturated alcoholic ammonia to 1 part of chloracetal, heating the mixture at 125—130° for 10 hours; 50 per cent. of the theoretical yield of the primary base can thus be obtained. If less ammonia is employed, large quantities of secondary and tertiary bases are formed.

Diacetalylthiocarbamide, $CS[NH\cdot CH_2\cdot CH(OEt)_2]_2$, is obtained on heating amidoacetal with a slight excess of carbon bisulphide on the water-bath. Hydrogen sulphide is evolved, and an oil is obtained which slowly solidifies. It crystallises from light petroleum in well-formed, transparent crystals, melts at 54°, and is extremely soluble in most organic solvents.

Acetalylcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, is obtained by warming amidoacetal hydrochloride in concentrated aqueous solution with a slight excess of potassium cyanate. It crystallises from hot water, melts at 105°, and is easily soluble in hot water and alcohol, moderately in cold water and chloroform, and sparingly so in ether and light petroleum.

μ-Imidazolone, $\begin{matrix} CO\cdot NH\cdot CH \\ | \quad\quad \| \\ NH\text{——}CH \end{matrix}$, is obtained by warming acetalylcarbamide in aqueous solution with a few drops of sulphuric acid. The sulphuric acid is precipitated by barium carbonate and the filtrate evaporated on the water-bath and allowed to crystallise. μ-Imidazolone is easily soluble in hot water, sparingly so in other solvents, and decomposes above the boiling point of concentrated sulphuric acid. The properties of the compound are in accordance with the formula given above and also with the tautomeric formula $\begin{matrix} HO\cdot C\cdot NH\cdot CH \\ \| \quad\quad | \\ N\text{——}CH \end{matrix}$. It has both feeble basic and acid properties, but the salts cannot be obtained pure. When alcohol is added to a solution of the hydrochloride, a solid salt is precipitated which is too hygroscopic to be analysed. The platinochloride behaves in a similar way. Gold chloride and ammoniacal silver solution are reduced with precipitation of the metal. The author could not obtain glyoxaline from this compound either by distillation over zinc dust or by reduction with hydriodic acid. When treated with phosphorus pentachloride, it is completely carbonised.

μ-Imidazolyl mercaptan, $\begin{matrix}HS\cdot C\cdot NH\cdot CH\\ \|\quad\quad\quad\|\\ N\text{——}CH\end{matrix}$.—An aqueous solution of equivalent quantities of amidoacetal and potassium thiocyanate is evaporated, the residue extracted with absolute alcohol, the alcohol distilled off, and the syrup which remains heated at 140°. A reaction then takes place with evolution of alcohol and the formation of μ-imidazolyl mercaptan. This melts at 222°, but begins to decompose at 210°, and is easily soluble in hot water and alcohol, less so in cold water and only sparingly in ether, benzene, and chloroform. It is easily soluble in alkalis, and forms salts both with acids and bases. The *hydrochloride* is crystalline and moderately soluble in alcohol. The *sulphate* is precipitated in crystals from alcoholic solutions. The *platinochloride* is brick-red and has the composition $(C_3H_4SN_2)_2PtCl_4$. The solution of the mercaptan gives precipitates with salts of the heavy metals.

μ-Imidazolylmethyl sulphide, $\begin{matrix}MeS\cdot C\cdot NH\cdot CH\\ \|\quad\quad\quad\|\\ N\text{——}CH\end{matrix}$, is obtained by allowing an alcoholic solution of the mercaptan and methyl iodide to remain for a day and then precipitating the solution with potash. It melts at 139°, boils at 251—252° without decomposition, is somewhat easily soluble in water, easily in most organic solvents, and gives well-crystallised salts with mineral acids. The *platinochloride* forms orange-yellow crystals, is sparingly soluble, and melts at 187° with decomposition. The *picrate* crystallises in beautiful, yellow needles, and melts at 186°. A crystalline silver derivative of the composition $C_4H_5SN_2Ag$ was also obtained.

Glyoxaline is obtained by warming imidazolyl mercaptan (6 grams) with 10 per cent. nitric acid (160 c.c.) on the water-bath and, after the first action is over, heating for half an hour at 100° and evaporating to dryness. The base is obtained by converting the product into the silver salt, decomposing this with hydrogen sulphide, and evaporating the aqueous solution; the syrupy residue distils at 257°, and solidifies in the receiver. It melts at 88°. The *aurochloride* forms yellow needles, is sparingly soluble in water and alcohol, and decomposes at 230°.

Acetalylparatolylthiocarbamide, $C_6H_4Me\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot CH(OEt)_2$, obtained from amidoacetal and paratolyl isothiocyanate, is an oil which slowly crystallises, melts at 54—56°, is precipitated as an oil from all organic solvents, and is very easily soluble. The *picrate*, $C_{14}H_{22}N_2SO_2.C_6H_2(NO_2)_3\cdot OH$, crystallises in lemon-yellow crystals, melts at 205°, and is sparingly soluble in all solvents.

ν-Paratolylimidazolyl-μ-mercaptan, $\begin{matrix}HS\cdot C\cdot N(C_7H_7)\cdot CH\\ \|\quad\quad\quad\quad\|\\ N\text{————}CH\end{matrix}$, is obtained by boiling the preceding compound with dilute hydrochloric acid for about an hour in a reflux apparatus. It crystallises in silvery leaflets, melts at 205° with incipient decomposition, and is sparingly soluble in cold water, more so in hot water It gives precipitates with salts of the heavy metals. The *platinochloride* is thrown down from an alcoholic solution as an orange, crystalline precipitate and has the composition $(C_{10}H_{10}N_2S)_2PtCl_4$.

Tolylimidazolyl methylsulphide.—When the preceding mercaptan dissolved in alcohol is treated with the equivalent quantity of methyl iodide and the mixture allowed to remain, a clear solution is obtained, from which ether precipitates white needles of the hydriodide of the above base. The *hydriodide* melts at 95°, and is very easily soluble in water and alcohol. The *base* is obtained by decomposing this salt with alkali; it is insoluble in water, easily soluble in most other solvents, melts at 90°, and sublimes in beautiful, fan-like crystals. It yields well crystallised salts with mineral acids. The *picrate* melts at 140°. The *platinochloride*, an orange-yellow, crystalline precipitate, is sparingly soluble in water, more easily so in alcohol. The base combines with methyl iodide to form a sulphinium base. The latter crystallises in white needles, melts at 162°, and is sparingly soluble in ether and cold water, easily so in hot water and alcohol.

ν-Paratolylimidazole, $\begin{matrix} CH\cdot N(C_7H_7)\cdot CH \\ \| \qquad\qquad \| \\ N - \!\!-\!\!-\!\!- CH \end{matrix}$, is obtained by warming tolylimidazolyl mercaptan with 16 times the quantity of 10 per cent. nitric acid on the water-bath, and decomposing the salt thus obtained with alkali. The product is extracted with ether, and the ethereal solution dried by potassium hydroxide and distilled; the base passes over at 285°, and solidifies in the receiver to pale-yellow crystals. It is sparingly soluble in water, very easily in other solvents, and has an intense mushroom-like odour. With mineral acids, it gives well-crystallised salts which are easily soluble in water. The *picrate* crystallises in golden needles, melts at 179°, and is insoluble in cold water and alcohol. The *platinochloride*, $(C_{10}H_{10}N_2)_2,H_2PtCl_6$, is a yellow, crystalline precipitate, and is sparingly soluble in water and alcohol. When concentrated silver nitrate is added to an alcoholic solution of the base, a white, crystalline compound of the composition

$$C_{10}H_{10}N_2,AgNO_3$$

is obtained. An *ammonium base* is formed when tolylimidazole dissolved in chloroform is allowed to remain for a day with methyl iodide; on adding ether to the solution, it is precipitated in slender, white needles. It melts at 90°, and is sparingly soluble in water, easily so in alcohol, chloroform, and benzene.

Acetalylmetaxylylthiocarbamide, $C_6H_3Me_2\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot CH(OEt)_2$, is obtained from amidoacetal and asymmetrical metaxylylthiocarbamide as a viscid oil, which solidifies in a few days. It melts at 53°, and is very easily soluble in most organic solvents, but only sparingly in water or light petroleum. The *picrate* crystallises in lemon-yellow needles, melts at 147—148°, and is sparingly soluble in water, light petroleum, cold alcohol, and ether, more easily in hot alcohol, chloroform, and benzene.

ν-Metaxylylimidazolyl-μ-mercaptan, $\begin{matrix} HS\cdot C\cdot N\cdot(C_8H_9)\cdot CH \\ \| \qquad\qquad \| \\ N - \!\!-\!\!-\!\!- CH \end{matrix}$, is obtained by the action of hydrochloric acid on the preceding mercaptan. It crystallises from hot water in nacreous leaflets, melts at 192°, and is sparingly soluble in cold water, more easily in cold alcohol, carbon bisulphide, and benzene, and easily in hot water and alcohol and in

chloroform and acetic acid. It yields precipitates with salts of the heavy metals. The *platinochloride*, $C_{11}H_{12}N_2S,PtCl_4$, is obtained in scarlet crystals, melts above 250°, is almost insoluble in water and ether, but somewhat soluble in alcohol and easily so in chloroform.

ν-Metaxylylimidazolyl-μ-methylsulphide, is obtained by treating the mercaptan with methyl iodide and decomposing the hydriodide with ammonia. It is an oil which cannot be distilled without decomposition. The base yields well-crystallised salts. The *hydriodide* melts at 165°, and is very easily soluble in water and alcohol, sparingly so in most other solvents. The *aurochloride* is obtained in greenish-yellow crystals. The *platinochloride* forms golden-yellow crystals, melts at 209° with decomposition, and is moderately soluble in alcohol. The *picrate* melts at 158—159°. The *iodide of the sulphinium base* is obtained by allowing the base to remain for a day with excess of methyl iodide. It forms white crystals, melts at 169—170°, and is easily soluble in chloroform, sparingly in other solvents.

ν-Metaxylylimidazole, $\begin{matrix}HC\cdot N(C_8H_9)\cdot CH\\ \|\qquad\qquad\|\\ N\text{———}CH\end{matrix}$, is obtained by oxidising the mercaptan with nitric acid, as an oil which distils at 279° without decomposition, and solidifies after a time, It melts at 32°, and is sparingly soluble in water, but very easily in most other solvents. The salts are easily soluble. The *aurochloride* forms greenish-yellow crystals, and melts at 164—165°. The *platinochloride* crystallises in long, slender, orange needles, sinters at 208°, melts with decomposition at a slightly higher temperature, and is very sparingly soluble in water, more easily so in alcohol. The *picrate* crystallises in deep-yellow needles, melts at 159°, and is sparingly soluble in most solvents, but more easily in chloroform.

Wohl and Marckwald (*Ber.*, **22**, 578) obtained a carbamide of the formula $NHPh\cdot CS\cdot NH\cdot CH_2\cdot CH(OH)\cdot OEt$, by treating acetylphenylthiocarbamide with concentrated sulphuric acid. With acids, this carbamide yielded salts which were not derived from the carbamide itself, but from a base formed from it by the withdrawal of the elements of water. This base has the formula $CS<^{-NPh-}_{NH\cdot CH_2}>CH\cdot OEt$, or $HS\cdot C<^{-NPh-}_{N\cdot CH_2}>CH\cdot OEt$, and when set free from its salts takes up water and is reconverted into the thiocarbamide. A similar carbamide of the formula $C_6H_3Me_2\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot CH(OH)\cdot OEt$ is obtained by dissolving acetalylmetaxylylthiocarbamide in well-cooled, concentrated sulphuric acid and pouring the mixture on to ice. On adding ammonia, an oil is obtained which dissolves on shaking with ether, and crystallises on evaporation of the solvent. It crystallises from dilute alcohol in white needles, melts at 94—95°, is insoluble in water, sparingly soluble in cold alcohol, but easily in hot alcohol and most other solvents. The carbamide dissolves in acids, but the salts were not obtained crystalline. With platinic chloride, it gives a scarlet, crystalline double salt. A *picrate*, which, however, as was to be expected, is derived from a base of the formula

$$\begin{matrix}CS\cdot N(C_8H_9)\cdot CH\cdot OEt\\ |\qquad\qquad|\\ NH\text{———}CH_2\end{matrix} \quad \text{or} \quad \begin{matrix}HS\cdot C\cdot N(C_8H_9)CH\cdot OEt\\ \|\qquad\qquad|\\ N\text{———}CH_2\end{matrix},$$

is obtained when picric acid is added to a hot, dilute alcoholic solution of the carbamide. It crystallises in lustrous, golden needles, melts at 143—144°, and is very easily soluble in chloroform, somewhat easily in benzene, but only sparingly in most other solvents.

α-Naphthylthiocarbimide is obtained by heating di-α-naphthylthiocarbamide with concentrated phosphoric acid. It crystallises from dilute alcohol in long needles, melts at 58°, and gradually reddens on exposure to air.

Acetalyl-α-naphthylthiocarbamide, obtained by treating the preceding compound with amidoacetal in alcoholic solution, forms slender, white crystals, melts at 112°, and is easily soluble in ether, benzene, light petroleum, and acetic acid, but more sparingly in cold alcohol.

ν α-Naphthylimidazole-μ-mercaptan, $\begin{matrix} HS\cdot C\cdot N(C_{10}H_7)\cdot CH \\ \| \qquad\qquad\quad \| \\ N \text{———} CH \end{matrix}$, forms white crystals, melts at 242° with decomposition, and is sparingly soluble in water and alcohol, but more easily in other solvents. The *silver derivative*, $C_{13}H_9N_2SAg$, is obtained as a white, crystalline precipitate on adding silver nitrate to an alcoholic solution of the mercaptan.

ν-α-Naphthylimidazolyl-μ-methylsulphide melts at 127°, is easily soluble in alcohol and ether, and yields well crystallised salts with mineral acids. The *hydriodide* is obtained as a syrup which slowly crystallises, separates as an oil from all solvents, and when boiled with water yields the free base. The *platinochloride*, $(C_{14}H_{12}N_2S)_2,H_2PtCl_6$, is obtained in yellow crystals which are sparingly soluble in water, alcohol, and ether. The *aurochloride* is a red, amorphous precipitate. The *picrate* crystallises from alcohol in long yellow needles, melts at 162°, and is sparingly soluble in water, alcohol, and ether.

ν-α-Naphthylimidazole, $\begin{matrix} CH\cdot N(C_{10}H_7)\cdot CH \\ \| \qquad\qquad\quad \| \\ N \text{———} CH, \end{matrix}$ distils undecomposed above the boiling point of mercury, melts at 62°, is insoluble in water, easily soluble in other solvents, and yields easily soluble and well crystallised salts. The *platinochloride* forms orange crystals, is sparingly soluble, and melts above 300°. The *picrate* crystallises in yellow needles, melts at 194—195°, and is sparingly soluble. The *methiodide*, $C_{13}H_{10}N_2,MeI$, melts at 195°, is insoluble in ether, and somewhat soluble in alcohol and water. E. C. R.

Formation of Oxazolines. By S. Gabriel and A. Neumann (*Ber.*, **25**, 2383—2388).—The method consists in eliminating a molecule of hydrogen chloride from a β-chlorethylimido-ether, when a μ-alkyloxazoline is formed.

Benzimido-β-chlorethyl ether, $NH{:}CPh\cdot O\cdot CH_2\cdot CH_2Cl$.—The *hydrochloride* of this compound is obtained by treating an ice-cold mixture of benzonitrile (5 grams) and ethylenechlorhydrin (4 grams) with dry hydrogen chloride for about half an hour. The solid crystalline mass thus obtained is ground in a mortar, washed with dry benzene, and dried, first over sulphuric acid, then at 60—70°; the yield is quantitative. It melts at 147—148° with decomposition. When warmed in aqueous solution, it is decomposed, and yields ammonium chloride and chlorethyl benzoate, $C_6H_5\cdot COOC_2H_4Cl$. The

latter, which is separated either by steam distillation or by extraction with ether, boils at 254—255° under a pressure of 749 mm. When the hydrochloride is heated alone above its melting point, it yields ethylene chloride and benzamide. The *picrate* of benzimidochlorethyl ether is obtained in sparingly soluble, yellow needles on adding a cold solution of picric acid to a cold, dilute, aqueous solution of the hydrochloride. It is dried over sulphuric acid, and decomposes on warming. The *platinochloride*, $(C_9H_{10}ONCl)_2,H_2PtCl_6$, forms orange-yellow scales, and melts at 180° to a reddish-brown liquid. The *free* benzimidochlorethyl ether is obtained in oily drops on adding an alkali to the cold aqueous solution of the hydrochloride, and can be extracted by shaking with ether; it is very easily decomposed. When the cold ethereal solution is allowed to evaporate over sulphuric acid, an oil is obtained which becomes semi-solid after a time, and consists of crystals of benzimidochlorethyl ether (m. p. 147—148°) and μ-phenyloxazoline. When the ethereal solution of benzimidochlorethyl ether is evaporated on the water-bath, it is converted almost quantitatively into β-chlorethylbenzamide, $C_2H_4Cl\cdot NH\cdot COPh$, which melts at 102—103°; and on boiling the latter compound with sodium hydroxide, a good yield of phenyloxazoline is obtained. A more convenient way of obtaining the phenyloxazoline, but one which gives a poorer yield, is to add normal soda (21 c.c.) to benzimidochlorethyl ether hydrochloride (2·2 grams), and, after diluting with water, to distil the mixture with steam. The distillate, which contains benzonitrile and phenyloxazoline, is mixed with hydrochloric acid, and after removing the benzonitrile by agitation with ether, the aqueous solution is saturated with alkali, and the phenyloxazoline extracted by ether.

Acetimido-β-chlorethyl ether, $NH{:}CMe\cdot O\cdot C_2H_4Cl$.—The *hydrochloride* is formed on saturating a well-cooled mixture of acetonitrile and ethylenechlorhydrin with dry hydrogen chloride; it is a viscous oil which deposits colourless needles after a time. The *picrate* crystallises in golden, six-sided leaflets, and melts at 106—107°. When the above oil is dissolved in water and the solution warmed, it is converted into chlorethyl acetate, $CH_3\cdot COOC_2H_4Cl$, which boils at 141—143° under a pressure of 754 mm. The same compound is obtained in small quantities when the hydrochloride is decomposed with soda and then subjected to steam distillation. The distillate also contains small quantities of methyloxazoline. The latter is separated as picrate, after extracting the chlorethyl acetate with ether, by adding picric acid to the aqueous solution. The *picrate* crystallises in yellow needles, and melts at 157—158°.

E. C. R.

Instability of Carboxyl in Phenolic Acids. By P. Cazeneuve (*Compt. rend.*, **115**, 182—185).—The conversion of gallic acid into pyrogallol at comparatively low temperatures, under the influence of aromatic amines (this vol., p. 1314), is a particular case of what appears to be a general property of phenolic acids, a number of which are now shown to be decomposed when heated with aniline.

Gallic acid splits up at 115°, protocatechuic acid at 180°, salicylic

acid at 220°, but benzoic acid is not affected. The stability of the acids decreases therefore as the number of phenolic hydroxyls increases.

Dibromosalicylic acid decomposes at 180°, dichlorosalicylic at 200°, dibromogallic acid at 80°, but tribromobenzoic acid is not affected. Orsellinic (methyldihydroxybenzoic) acid splits up at 110°, and dibromorsellinic acid loses carbonic anhydride when heated in water to 100°, and presumably, therefore, at a lower temperature when heated in aniline. Thus the stability of the acids is decreased by the nucleal substitution of halogen or alkyl.

Finally, salicylic acid is less stable than parahydroxybenzoic acid, and this in turn than the meta-acid, which is scarcely affected when heated with aniline in a sealed tube at 240°. Jn. W.

Orthoparadinitrophenylglycollic Acid. By L. Pratesi (*Gazzetta*, **22**. i, 242—250.—The author has previously mentioned that when phenylglycollic acid is nitrated with nitric acid of 48° Baumé, the product is 2 : 4-*dinitrophenylglycollic* acid. It crystallises from water in large, colourless, or pale, yellowish-green prisms, melts at 147—148° in the air, and at 86° under water. It is sparingly soluble in cold water (1 part in 353 of water at 21°), moderately in cold alcohol, benzene, ether, and acetic acid. It is converted by potash into the corresponding dinitrophenol melting at 113—114°. The ammonium salt crystallises in colourless plates containing $\frac{1}{2}$ mol. H_2O, and is very soluble in water; it gradually loses weight in a vacuum. The *potassium* salt contains $\frac{1}{2}$ mol. H_2O; it is almost colourless, very soluble in water, turns yellow at 107°, and decomposes at a higher temperature. It deflagrates when rapidly heated. The *sodium* salt contains 1 mol. H_2O; it is very soluble in water, and deflagrates on heating. The *barium* salt crystallises in thin plates containing $3\frac{1}{2}$ mols. H_2O; it is moderately soluble in boiling water, and decomposes when heated above 100°. The *copper* salt contains 5 mols. H_2O; the *silver* salt is anhydrous. The *ethyl* derivative is a white, crystalline compound, which melts at 77—78°, and is sparingly soluble in cold alcohol. The *methyl* derivative melts at 73°. The *amide* is obtained by leaving either the methyl or ethyl derivative in contact with concentrated ammonia for 24 hours. It crystallises from alcohol in white needles melting at 182—184°. It is moderately soluble in boiling alcohol, but insoluble in water. With nitrous acid, it yields 2 : 4-dinitrophenylglycollic acid.

Phenylglycollic, paracresolglycollic, thymolglycollic, salicylglycollic, and resorcinoldiacetic acids are readily converted into the corresponding phenols by fusing the acid (1 part) with potash (4 parts) and water (1 part). The yield is in general almost theoretical, but if the heating is carried too far, the lateral groups become oxidised. Ortho- and para-nitrophenylglycollic acids are much more readily hydrolysed. S. B. A. A.

Derivatives of Phenylglycocine and Orthotolylglycocine. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **25**, 2270—2280).—A good yield of ethyl anilidoacetate (Meyer, this Journal, 1876, i, 372)

is obtained from ethyl chloracetate (100 grams) by heating it on the water-bath for an hour with aniline (150 grams). After repeated crystallisation from light petroleum, it melts at 58°, and boils at 273—274°. It gives phenylglycocine on treatment with aqueous alkali. When phenylglycocine is treated at the ordinary temperature with acetic anhydride, acetylphenylglycocine, melting at 194—195° (compare Rebuffat, Abstr., 1887, 1108; Paal and Otten, Abstr., 1890, 1415), is obtained; whilst if the reagents are heated together in an oil-bath at 160—180°, a small quantity of diphenyl-$\alpha\gamma$-diketopiperazine (Abstr., 1890, 1332) is also formed.

Phenylimidodiacetic anhydride, $NPh<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>O$, is obtained by heating phenylimidodiacetic acid (2 grams) with acetic anhydride (3 grams) on the water-bath; when crystallised from benzene and acetone, it forms tablets, melts at 148°, and is sparingly soluble in light petroleum; water converts it into the acid, and when heated with aniline at 150° the anilide melting at 211—213° (Abstr., 1889, 1014) is produced. Dimethylparatoluidine (Hübner, *Annalen*, **224**, 336) is formed when phenylimidodiacetic acid is distilled.

Diphenylhydantoïn, $NPh<\begin{matrix}CH_2CO\\CO\cdot NPh\end{matrix}$, is prepared by dropping phenylglycocinanilide (5 grams) into a solution of sodium (0·5 gram) in absolute alcohol (12 grams), and adding carbonyl chloride (4·5 grams) dissolved in benzene to the cooled mixture; the product is then shaken with water, and the oil which separates, probably the salt $NHPh\cdot CO\cdot CH_2\cdot NPh\cdot COOEt$, is converted into the hydantoïn by means of concentrated aqueous potash; on the addition of acid, it separates as an oil, which subsequently solidifies. It crystallises from alcohol in colourless plates, and melts at 139°.

Ethyl orthotoluidoacetate (Ehrlich, Abstr., 1883, 593) is obtained by heating ethyl chloracetate with orthotoluidine for $1\frac{1}{2}$ hours on the water-bath; it is a colourless oil, boiling at 281° (746 mm.), and having a sp. gr. of 1·058 at 20°/20°. When tolylglycocinetoluidide (Ehrlich, *loc. cit.*) is distilled, orthoditolylcarbamide is formed. If dissolved in benzene and treated with a solution of carbonyl chloride (2 mols.) in the same solvent, a white precipitate separates. On heating this at 170—175° for three hours, and then distilling in a current of steam, a residue is left, which is insoluble in alcohol and ether; when this is dissolved in chloroform and precipitated with ether, *orthoditolylhydantoïn* is obtained as a colourless, crystalline powder, melting at 270° ~275°.

Acetylorthotolylglycocine, $C_6H_4Me\cdot NAc\cdot CH_2\cdot COOH$, is formed when orthotolyglycocine (5 grams) is heated with acetic anhydride (4 grams) for two hours, in a reflux apparatus on an oil-bath at 180°; it crystallises from dilute alcohol in colourless, elongated tables, melts at 210—212°, and is sparingly soluble in cold ether, and in hot and cold water, readily in hot 50 per cent. alcohol and glacial acetic acid.

Diorthotolyl-$\alpha\gamma$-diketopiperazine (Abstr., 1889, 1012) is produced by heating orthotolylglycocine with acetic anhydride for four hours at 138°. It is not attacked by zinc and hydrochloric acid, by sodium amalgam and acetic acid, or by alcoholic ammonia at 150°, but it is

converted into orthotolylglycocine when treated with a solution of sodium in amyl alcohol.

Ammonium orthotolylimidodiacetate, $C_6H_4Me{\cdot}N(CH_2{\cdot}COONH_4)_2$, is obtained by saturating an alcoholic solution of the acid with ammonia; it melts at 158—160° with the evolution of ammonia and alcohol, and is readily soluble in water, sparingly in cold alcohol, but readily so in the hot liquid.

Orthotolylimidodiacetamide, $C_6H_4Me{\cdot}N(CH_2{\cdot}CONH_2)_2$, is formed when the acid is dissolved in aqueous ammonia, and the solution evaporated; it forms white, lustrous leaflets, melts at 163—164°, and is sparingly soluble in cold water and alcohol, readily so in the hot liquids, as well as in ether.

Orthotolylimidodiacetimide, $C_6H_4Me{\cdot}N<\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CO\end{matrix}>NH$, is produced by heating ammonium orthotolylimidodiacetate in an oil-bath at 165° for 4—5 hours; it crystallises from alcohol in white, lustrous prisms, melts at 145—146°, and is sparingly soluble in water and ether. A. R. L.

Paratolylglycocine and its Derivatives. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **25**, 2280—2290).—Ethyl paratoluidoacetate (Meyer, this Journal, 1176, i, 402) is prepared by heating ethyl chloracetate (100 grams) with paratoluidine (175 grams) for an hour on the water-bath; it crystallises in the asymmetric system, $a : b : c = 0{\cdot}3878 : 1 : 0{\cdot}2595$.

Schwebel (*Ber.*, **10**, 2407) described a compound melting at 166—168° as paratolylglycocine, which he obtained by Meyer's method (*loc. cit.*); later Schwebel (*Inaug. Diss.*, Berlin, 1878) isolated an isomeride melting at 118—119°, which he supposed to be orthotolylglycocine. Meyer, however, subsequently showed (*Ber.*, **14**, 1323) that the latter was not orthotolylglycocine; he considered the compound of higher melting point to be paratolylglycocine, and that of lower melting point to be a polymeride (see below). Various observers have from time to time noted the abnormal behaviour of the so-called paratolylglycocine (compare, for example, Heumann, Abstr., 1891, 928). The authors now find that when the above described ethyl salt is treated with concentrated aqueous potash, and the solution cautiously neutralised, the compound melting at 118—119° is precipitated; it gives the indigo reaction on heating it with potassium hydroxide at 300°, and is accordingly the true paratolylglycocine. The so-called paratolylglycocine melting at 166—168° is obtained when chloracetic acid (25 grams) and paratoluidine (57·5 grams) are suspended in water (800 c.c.), and the mixture boiled in a reflux apparatus for three hours; it is recrystallised from water, and a certain quantity of paratolylglycocine may be isolated from the aqueous mother liquor. The compound does not give the indigo reaction, but when it is heated with sodium carbonate solution, paratoluidine separates, and paratolylimidodiacetic acid (see below) can be isolated from the alkaline solution; it has, therefore, the constitution, $C_6H_4Me{\cdot}N<\begin{matrix}CH_2{\cdot}COOH\\CH_2{\cdot}COO{\cdot}NH_3{\cdot}C_6H_4Me\end{matrix}$, assigned by

Meyer to the true paratolylglycocine (see above). It also gives *paratolylimidodiacetic ditoluide*, $C_6H_4Me{\cdot}N(CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me)_2$, melting at 213—215°, when heated with paratoluidine at 200°.

Paratolylimidodiacetic acid, $C_6H_4Me{\cdot}N(CH_2{\cdot}COOH)_2$, is prepared by heating together on the water-bath paratolylglycocine (10 grams), chloracetic acid (6 grams), and anhydrous sodium carbonate (10 grams), in aqueous solution. On adding concentrated hydrochloric acid to the hot solution until the precipitate at first produced redissolves, and allowing it to cool, the compound separates in lustrous needles. It loses water at 100°, and melts completely at 120°; it is soluble in most solvents except light petroleum, and its crystals contain $\frac{1}{2}$ mol. H_2O.

Paratolylglycocine, when treated with acetic anhydride, gives the acetyl derivative described by Paal and Otten (Abstr., 1890, 1415). The compounds previously obtained by the authors (Abstr., 1890, 1284) by the action of acetic anhydride on the supposed paratolylglycocine (m. p. 166—168°) are now found to be acetylparatoluidine (m. p. 147°) and paratolylimidodiacetic monamide (m. p. 222°). Diparatolyl-$\alpha\gamma$-diketopiperazine, melting at 254—255° (Abenius, Abstr., 1890, 269), is obtained, together with *diparatolyl-$\alpha\delta$-diketopiperazine*, on heating paratolylglycocine; the δ-compound is separated from the $\alpha\gamma$-compound by means of its greater solubility in alcohol: it melts at 185°, and gives paratolylimidodiacetic monotoluidide (Abstr., 1890, 1285) on treatment with alcoholic potash, and the *amide*, $C_6H_4Me{\cdot}N{<}\begin{matrix}CH_2{\cdot}CO{\cdot}NH_2\\CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me\end{matrix}$, identical with the compound previously described as paratolylglycinimide (Abstr., 1890, 1284), on boiling with alcoholic ammonia.

Diparatolylhydantoïn, $C_6H_4Me{\cdot}N{<}\begin{matrix}CH_2{\cdot}CO\\CO{\cdot}N{\cdot}C_6H_4Me\end{matrix}$, is obtained when paratolylglycocine toluidide (5 grams) is treated with a 20 per cent. solution of carbonyl chloride (25 grams), and the mixture heated at 140° for an hour; when the residue left on evaporating the solvent is crystallised from alcohol, the pure compound is obtained in colourless leaflets melting at 175°; it is sparingly soluble in light petroleum, but readily so in other solvents.

Chloracetylparatolylglycocine toluidide,

$$C_6H_4Me{\cdot}N(CO{\cdot}CH_2Cl){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me,$$

is produced on mixing paratolylglycocine toluidide dissolved in benzone with an equal weight of chloracetic chloride; it forms slender, white needles, melts at 158°, and is readily soluble in alcohol, but insoluble in light petroleum. A. R. L.

Derivatives of α-Amidopropionic Acid. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **25**, 2298—2313).—Of the three diphenyl-$\alpha\gamma$-dimethyl-$\beta\delta$-diketopiperazines (Nastvogel, Abstr., 1890, 1160), that melting at 183·5° is, in accordance with Bischoff's scheme for distinguishing the geometrically isomeric substituted succinic acids, the para-modification, and that melting at 172—173° the anti-modification, since the former is convertible into the latter (*loc. cit.*; see

also below). When α-bromopropanilide melting at 99° (45·6 grams) is heated on the water-bath for four hours with potassium hydroxide (11·2 grams) dissolved in alcohol (200 c.c.), *α-ethoxypropanilide*, $NHPh{\cdot}CO{\cdot}CHMe{\cdot}OEt$, which crystallises in white, nodular aggregates of needles and melts at 62—63°, is obtained, together with the above-mentioned para- and anti-diphenyldimethyldiketopiperazines. When paradiphenyl-αγ-dimethyl-βδ-diketopiperazine (5 grams) is boiled with 10 per cent. aqueous potash (150 c.c.) and the acid obtained on acidifying the solution heated at 120°, antidiphenyl-αγ-dimethyl-βδ-diketopiperazine is formed, but Nastvogel's diphenyldimethyldiketopiperazine melting at 144—146°, which is perhaps a structural isomeride, is not present.

Ethyl α-orthotoluidopropionate, $C_6H_4Me{\cdot}NH{\cdot}CHMe{\cdot}COOEt$, is formed on heating ethyl α-bromopropionate with orthotoluidine at 100°; it is a yellowish oil of sp. gr. 1·047 at 20°/20°, and boils at 277—278°. The corresponding acid has been described by Gerson (Abstr., 1887, 260); the *acetyl derivative*, $C_6H_4Me{\cdot}NHAc{\cdot}CHMe{\cdot}COOH$, crystallises in white leaflets, and melts at 177°.

Ethyl α-paratoluidopropionate crystallises in large tables, and melts at 35°. The *acid* obtained from it by hydrolysis with potash forms silvery scales, melts at 158°, and is soluble in both acids and alkalis; the *acetyl derivative* melts at 166°. When the acid is quickly distilled, it decomposes for the most part into acetylparatoluidine melting at 217°; if, however, it is slowly heated at 200—210° in a current of carbonic anhydride, or, better, with acetic anhydride, the portion of the product insoluble in alkalis consists of two isomeric *diparatolyl-αγ-diketopiperazines*, $C_6H_4Me{\cdot}N<\begin{matrix}CHMe{\cdot}CO\\CO{\cdot}CHMe\end{matrix}>N{\cdot}C_6H_4Me$; of these, the para-modification crystallises in colourless, translucent needles, melts at 248°, and is very easily soluble in chloroform, whilst the anti-modification forms prisms, melts at 191—195°, and is somewhat less soluble in chloroform.

Ethyl α-naphthylidopropionate, obtained by heating ethyl α-bromopropionate with α-naphthylamine at 165°, crystallises from alcohol in small, nodular crusts, and melts at 65·5°. The corresponding *acid*, obtained by hydrolysing the ethyl salt with potash, as well as by heating together α-bromopropionic acid, α-naphthylamine, and water, crystallises from alcohol in small, lustrous leaflets, and melts at 160—161°; on distilling it, ethyl-α-naphthylamine, boiling at 303°, passes over.

Ethyl β-naphthylidopropionate is produced, together with ββ-dinaphthylamine, when ethyl α-bromopropionate is heated at 165° for two hours with β-naphthylamine; it crystallises in prisms, and melts at 84°. *β-Naphthylido-α-propionic acid* is obtained from the ethyl salt, and also by heating together α-bromopropionic acid, β-naphthylamine, and water; it melts at 170—171°, and is insoluble in cold water, but soluble in hot alcohol. When the acid is distilled, ethyl-β-naphthylamine (see Bamberger and Müller, Abstr., 1889, 888) passes over at 307—310°. On boiling the acid with acetic anhydride, the *acetyl derivative* melting at 197—199° is obtained from the portion soluble in alkali, whilst *β-dinaphthyl-αγ-dimethyl-βδ-diketopiperazine*,

$C_{10}H_7 \cdot N < \begin{matrix} CHMe \cdot CO \\ CO \cdot CHMe \end{matrix} > N \cdot C_{10}H_7$, melting at 269°, is isolated from the portion insoluble in alkali. A. R. L.

Derivatives of α-Amidobutyric Acid. By C. A. Bischoff and N. Mintz (*Ber.*, **25**, 2314—2325).—When α-anilidobutyric acid (Duvillier, Abstr., 1881, 87) is quickly distilled, propylaniline passes over. *Acetanilidobutyric acid*, NPhAc·CHEt·COOH, is obtained when α- anilidobutyric acid (5 grams) is heated in a reflux apparatus on the water-bath with acetic chloride (8 c.c.) ; the product is dissolved in aqueous sodium carbonate, the solution extracted with ether and acidified with hydrochloric acid, when the acid separates as a resinous mass, but after remaining for a week in the cold it becomes crystalline. It separates slowly from its solution in benzene in prisms, melts at 118°, is sparingly soluble in light petroleum and cold water, but readily in hot water and most other solvents. The two diphenyl-αγ-diethyl-βδ-diketopiperazines melting at 260° and 145°, which are described by Nastvogel (Abstr., 1890, 1160), may be distinguished as the para- and anti-modifications respectively.

Ethyl α-orthotoluidobutyrate, $C_6H_4Me \cdot NH \cdot CHEt \cdot COOEt$, prepared by heating orthotoluidine with ethyl α-bromobutyrate on the water-bath for 4—5 hours, is a bright-yellow liquid of sp. gr. 1·019 at 20°/20°, boiling at 278°. The corresponding *acid* forms long prisms melting at 84°, gives an *acetyl* derivative, $C_6H_4Me \cdot NAc \cdot CHEt \cdot COOH$, melting at 114—116°, and when distilled yields propylorthotoluidine boiling at 230°.

Ethyl α-paratoluidobutyrate, formed by heating paratoluidine with ethyl α-bromobutyrate at 105°, boils at 278—280°, and has a sp. gr. at 20°/20° = 1·011. The corresponding acid crystallises in leaflets, melts at 153—156°, and gives propylparatoluidine (Hori and Morley, Trans., 1891, 35) on distillation ; when heated with acetic anhydride in a sealed tube at 160°, the acid yields an *acetyl* derivative melting at 149°, whilst from a portion of the product insoluble in alkali two isomeric *diparatolyl-αγ-diethyl-βδ-diketopiperazines*, melting at 256° and 204—210° respectively, are isolated.

Ethyl α-naphthylidobutyrate, $C_{10}H_7 \cdot NH \cdot CHEt \cdot COOEt$, produced by heating ethyl α-bromobutyrate with α-naphthylamine at 165°, crystallises from alcohol in white, silky needles melting at 80°. The corresponding acid crystallises from dilute alcohol in small tablets, melts at 126° with the evolution of gas, and, when heated at 200°, gives *propyl α-naphthylamine*, boiling at 316—318°, the *acetyl derivative* of which melts at 93—94°.

Ethyl β-naphthylidobutyrate is obtained, together with β-dinaphthylamine (m. p. 172°), when ethyl α-bromobutyrate is heated with β-naphthylamine at 165° ; it crystallises in prisms, melts at 69°, and boils at 264° (43 mm.). The corresponding acid melts at 158°, and when distilled yields *propyl-β-naphthylamine*, boiling at 322—324°. A. R. L.

Anilidoisobutyric Acids. By C. A. Bischoff and N. Mintz (*Ber.*, **25**, 2326—2334).—Ethyl anilidoisobutyrate, melting at 30° (Abstr., 1891, 828), is the β-compound, $NHPh \cdot CH_2 \cdot CHMe \cdot COOEt$,

and not the α-derivative as stated; its formation from aniline and ethyl α-bromisobutyrate is in harmony with Bischoff's dynamical hypothesis (Abstr., 1890, 723). When the product of the action is heated with potash in a current of steam, β-anilidoisobutyric acid (Tiemann, Abstr., 1883, 1993) passes over, together with one-fifth of its weight of the α-acid (see below), and can be separated by fractional precipitation with hydrochloric acid. *β-Acetanilidoisobutyric acid*, $NPhAc\cdot CH_2\cdot CHMe\cdot COOH$, melts at 174°. When β-anilidoisobutyric acid is distilled, aniline and a *lactone* melting at 120° are formed; the latter has one of the formulæ $NPh<\begin{matrix}CH_2\cdot CHMe\cdot CO\\ CO-CMe_2-O\end{matrix}$ or $NPh<\begin{matrix}CH_2\cdot CHMe\cdot CO\\ CO\cdot CHMe\cdot CH_2\end{matrix}>O$.

α-Anilidoisobutyric acid melts at 140—142°, and gives isopropylaniline (Pictet and Crépieux, Abstr., 1888, 689) on distillation.

A. R. L.

Toluidoisobutyric Acids. By C. A. Bischoff and N. Mintz (*Ber.*, **25**, 2334—2345).—When orthotoluidine (250 grams) is heated on the water-bath with ethyl α-bromisobutyrate (195 grams), and the mixture subsequently heated at 150—160° for nine hours, the portion of the product boiling between 250° and 295° solidifies on being cooled, and separates from ether in asymmetrical crystals, $a:b:c = 0{\cdot}8623:1:0{\cdot}5041$, melting at 57°, and having the composition of an ethyl orthotoluidoisobutyrate. When this compound is heated with potash in a current of steam, two acids, melting at 60—62° and at 108—110° respectively, are isolated by fractional precipitation with hydrochloric acid. The former is probably α-orthotoluidobutyric acid; the latter is the corresponding β-acid, and yields an *acetyl derivative*, $C_6H_4Me\cdot NAc\cdot CH_2\cdot CHMe\cdot COOH$, which melts at 219°, and is sparingly soluble in hot ether. On distillation, orthotoluidine and the *lactone* $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot CHMe\\ CO\cdot C_3H_6\cdot O\end{matrix}>CO$, melting at 95°, are obtained.

When paratoluidine (260 grams) is heated at 160—170° for 10 hours with ethyl α-bromisobutyrate, the portion of the product boiling below 295° consists of a compound having the composition of an ethyl paratoluidoisobutyrate, whilst the small portion boiling above 295° is the lactone (m. p. 170°) described below. The ethyl salt solidifies on being cooled, and crystallises from ether in monosymmetric crystals, $a:b:c = 0{\cdot}81055:1:0{\cdot}67955$; $\beta = 79°\ 30'$; and melts at 36°. When treated with potash in a current of steam, two acids are isolated on fractional precipitation with hydrochloric acid. *β-Paratoluidoisobutyric acid* melts at 194—196°, gives an *acetyl* derivative,

$$C_6H_4Me\cdot NAc\cdot CH_2\cdot CHMe\cdot COOH,$$

melting at 206°, and decomposes on distillation into paratoluidine and the *lactone*,

$$C_6H_4Me\cdot N<\begin{matrix}CH_2-CHMe\cdot CO\\ CO\cdot CHMe\cdot CH_2\cdot O\end{matrix}\quad\text{or}\quad C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot CHMe\\ CO\cdot CMe_2\cdot O\end{matrix}>CO,$$

melting at 170°. *α-Paratoluidoisobutyric acid* melts at 149—150°, and

on distillation isopropylparatoluidine (compare Hori and Morley, Trans., 1891, 34) passes over at 230—231°. It yields an acetyl derivative melting at 144—146°. A. R. L.

Synthesis of Unsaturated Nitriles. By E. Fiquet (*Bull. Soc. Chim.* [3], **7**, 11—13).—A mixture of benzaldehyde with cyanacetic acid in molecular proportion is heated at 180°, and the crystalline mass which forms on cooling is treated with alcohol. The product, *benzylidenecyanacetic acid*, $C_{10}H_7NO_2$, melts at 180°. It does not combine with bromine, and, when treated with potassium hydroxide, yields benzaldehyde and potassium acetate and carbonate, with evolution of ammonia; if heated above its melting point, it gives off carbonic anhydride and yields cinnamonitrile, distilling at 252—254°. From these reactions, the author infers that benzylidenecyanacetic acid has the constitution CHPh:C(CN)·COOH, which the determination of the molecular weight by Raoult's method confirms. Metatoluic, cinnamic, and acetic aldehydes yield analogous compounds.

This acid differs from its isomeride described by Carrick (Abstr., 1890, 1270; this vol., p. 1086), in that the latter has entirely different reactions. T. G. N.

Xylenedisulphonic Acids. By E. Pfannenstill (*J. pr. Chem.* [2], **46**, 152—157).—Metaxylenedisulphonic acid [$Me_2 : (SO_3H)_2 = 1 : 3 : 2 : 4$] was prepared by Wischin (Abstr., 1891, 73) by the direct sulphonation of metaxylene. The author has prepared it from crystalline metaxylenesulphonic acid [$Me_2 : SO_3H = 1 : 3 : 4$] by heating it (3 parts) with chlorosulphuric acid (4 parts) at 150°, neutralising it with chalk, converting it into potassium salt, and then into the disulphonic chloride in the usual manner. The acid is obtained on heating the disulphonic chloride with water in a sealed tube at 140°. The *potassium* (with 2 mols. H_2O), *sodium* (with 3 mols. H_2O), *ammonium*, *barium* (with 3 mols. H_2O), *lead* (with 3 mols. H_2O), *magnesium*, *zinc*, *cadmium*, and *copper* salts were prepared. The *ethyl* salt crystallises in laminæ, and is nearly insoluble in water, but soluble in alcohol. The disulphonic chloride melts at 129°, and the amide at 249°. The dihydroxymetaxylene obtained by fusing the potassium salt with potassium hydroxide melts at 149—150° (Wischen, *loc. cit.*).

Metaxylenedisulphonic acid [$Me_2 : (SO_3H)_2 = 1 : 3 : 2 : 5$], corresponding with the uncrystallisable metaxylenesulphonic acid ($Me_2 : SO_3H = 1 : 3 : 2$; this Journal, 1877, ii, 601), is prepared from crude xylene by shaking it with strong sulphuric acid, which dissolves the meta- and ortho-xylene; after separating the crystallisable acid as far as possible, the sulphuric acid mother liquor, containing the uncrystallisable acid, is neutralised with barium hydroxide, and the barium salt further sulphonated with chlorosulphuric acid as above; the product is then treated with ether, whereby the metaxylenedisulphonic chlorides may be separated, the crystalline variety being less soluble. The *acid* crystallises in needles, and its *potassium*, *barium*, and *lead* salts are easily soluble and easily crystallised. The *chloride* is a brown, viscid oil which does not crystallise. The *amide*

is more soluble in water than that of the crystalline acid, and melts at 210°.

Orthoxylenedisulphonic acid can be prepared in a similar manner; it could not be crystallised. The *potassium* salt, with x mols. H_2O, the *barium* salt, with 3 mols. H_2O, and the *lead* salt, with 3 mols. H_2O, were prepared.

The *disulphonic chloride* crystallises in prisms, melts at 79°, and dissolves in ether, chloroform, and carbon bisulphide. The *amide* melts at 239°, and is sparingly soluble in water. The corresponding dihydroxyorthoxylene was prepared, but its constitution was not settled; 4 : 6 is the most probable orientation of the sulphonic groups in the sulphonic acid.

A paraxylenedisulphonic acid has been prepared by Holmes (Abstr., 1891, 1374); it agrees in the main with that prepared by the author, who, however, finds that the disulphonic chloride melts at 74—75° (not 72—74°), that the amide melts at 250° (not 294°), and that the barium salt crystallises with 3 mols. H_2O. A. G. B.

Nitro-β-naphthols. By F. Gaess (*J. pr. Chem.* [2], **46**, 160).—By a printer's error, the orientation of the nitro-β-naphthols described in the author's last paper (this vol., p. 1229), was wrongly given; "1′ : 2′-nitronaphthol" should read "1′ : 2-nitronaphthol," and "2 : 2′-nitronaphthol" should read "3′ : 2-nitronaphthol."

A. G. B.

Derivatives of Naphthylglycocines. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **25**, 2290—2298).—Ethyl α-naphthylidoacetate, $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}COOEt$, is prepared by heating ethyl chloracetate (50 grams) and α-naphthylamine (99 grams) with anhydrous sodium carbonate (45 grams) in a reflux apparatus, adding water, extracting with ether, and fractionating under diminished pressure; it is a yellowish oil, insoluble in water, but miscible with alcohol; it boils at 244° (5 mm.).

α-Naphthylglycocine-α-naphthylidoacetic acid,

$$C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}N(C_{10}H_7){\cdot}CH_2{\cdot}COOH,$$

is obtained when α-dinaphthyl-αγ-diketopiperazine (Abstr., 1890, 1309) is heated with alcoholic potash; it decomposes easily, melts at 180°, and is sparingly soluble in cold water and light petroleum, readily in ether and hot alcohol. Acetyl-α-naphthylglycocine (Forte, Abstr., 1890, 901) is prepared from α-naphthylglycocine and acetic chloride at the ordinary temperature.

The compound obtained by heating α-naphthylglycocine at 273° melts at 275°; it is not a piperazine derivative, but has, perhaps, the constitution $(C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CO)_2O$; it gives α-naphthylglycocine on heating with sodium and amyl alcohol.

α-Naphthylglycocinenaphthylide, $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, is prepared by heating α-naphthylglycocine with α-naphthylamine in molecular proportion in an oil-bath at 200°, removing the resinous bye-products by treatment with boiling ether, and crystallising the

residue from alcohol. It forms small needles, melts at 160°, is insoluble in cold ether, and gives α-dinaphthyl-αγ-diketopiperazine (*loc. cit.*) when treated with sodium ethoxide and ethyl chloracetate.

Ethyl β-naphthylidoacetate, prepared in the same way as the α-compound, melts at 88°, and gives β-naphthylglycocine when heated with alcoholic potash for 12 hours on the water-bath.

β-Dinaphthyl-αγ-diketopiperazine, when fused with potash, yields β-naphthylglycocine, and, when dissolved in glacial acetic acid and treated with potassium nitrite, it gives a compound, $C_{24}H_{18}N_2O_2$, melting above 360°.

Acetyl-β-naphthylglycocine, $C_{10}H_7{\cdot}NAc{\cdot}CH_2{\cdot}COOH$, is obtained by heating β-naphthylglycocine with acetic anhydride at 150°; it crystallises in needles, melts at 172°, and is readily soluble in alcohol, but only sparingly so in benzene. A. R. L.

Derivatives of α- and β-Naphthylidoisobutyric Acids, &c. By C. A. Bischoff and N. Mintz (*Ber.*, **25**, 2345—2354).—*Ethyl α-naphthyl-β-amidoisobutyrate*. $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CHMe{\cdot}COOEt$, is thus prepared:—Ethyl α-bromisobutyrate (100 grams), α-naphthylamine (73·3 grams), and anhydrous sodium carbonate (27·2 grams) are heated together at 175—200°, the solid product is extracted with ether, and the extract distilled; the portion passing over between 200° and 220° under a pressure of 15 mm. solidifies, and can be crystallised from alcohol, when it forms rhombic tables melting at 76·5°. The corresponding *acid* obtained on hydrolysing the salt with potash, and also by boiling a mixture of α-bromisobutyric acid (50 grams), α-naphthylamine (86 grams), and water (1 litre), crystallises from alcohol in six-sided tables, melts at 146°, and is almost insoluble in water; on distillation, α-naphthylamine and a *lactone*, melting at 107°, are isolated. The *acetyl* derivative,

$$C_{10}H_7{\cdot}NAc{\cdot}C_3H_6{\cdot}COOH,$$

melts at 246°.

Ethyl β-naphthyl-β-amidoisobutyrate, $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CHMe{\cdot}COOEt$, prepared by heating a mixture of ethyl α-bromobutyrate (200 grams), β-naphthylamine (146 grams), and anhydrous sodium carbonate (54 grams) for five hours at 170°, is isolated from the portion of the product passing over at 215—235° (11 mm.), which solidifies and crystallises from alcohol in translucent truncated prisms, and melts at 58°. When the ethyl salt is hydrolysed in the usual manner, there is some difficulty in isolating the acid; this is best prepared in the same way as the acid derived from α-naphthylamine (see above) from α-bromisobutyric acid, β-naphthylamine, and water. It crystallises from alcohol in leaflets, melts at 188°, and is almost insoluble in water; it gives an *acetyl derivative*, $C_{10}H_7{\cdot}NAc{\cdot}C_3H_6{\cdot}COOH$, which melts at 188°, and is sparingly soluble in water.

β-Anilidopropionic acid (*phenyl-β-alanine*), $NHPh{\cdot}C_2H_4{\cdot}COOH$, is obtained when β-iodopropionic acid (20 grams), aniline (19 grams), and water (20 c.c.) are heated together in a reflux apparatus; after warming with dilute hydrochloric acid, the liquid is rendered alkaline, and a current of steam driven through the solution; on now

adding hydrochloric acid, an oil separates, which, when dissolved in ether, slowly deposits crystals. These, after recrystallisation from a mixture of chloroform and light petroleum, form lustrous leaflets which melt at 59—60°, and decompose with the evolution of aniline if heated above their melting point.

β-Paratoluidopropionic acid (*paratolyl-β-alanine*),

$$C_6H_4Me\cdot NH\cdot C_2H_4\cdot COOH,$$

melts at 86°. A. R. L.

The Camphor Group. By U. Alvisi (*Gazzetta*, **22**, i, 265—275).—An attempt made to prepare a cyanhydrin from camphor was unsuccessful, hydrogen cyanide having no action on camphor either at the ordinary temperature or at 60—80°, or even when in the nascent condition. The monobromocamphor, melting at 144°, prepared by Cazeneuve (Abstr., 1889, 1204) by the action of hypobromous acid on camphor could not be isolated, the product of the reaction after purification containing 6 to 11 per cent. of bromine. On boiling α-dibromocamphor with concentrated aqueous potash, it is in great part converted into the monobromocamphor melting at 76°. It further appears that in the conversion of α-dibromocamphor into monobromocamphor by heating it with potassium permanganate in alkaline solution, the action of the permanganate is quite secondary, being limited to the formation of some resinous and other bye-products.

On treating dibromocamphor (1 mol.) with phenylhydrazine (2 mols.), the product consists of the hydrazone, $N_2H_2Ph\cdot C_{10}H_{14}:N_2HPh$, monobromocamphor, ammonium bromide, aniline hydrobromide, phenylhydrazine hydrobromide, benzene, and nitrogen.

S. B. A. A.

Methyl Camphocarboxylates, Methylcamphor, and Azo-derivatives of Cyanocamphor. By J. Minguin (*Compt. rend.*, **115**, 120—122).—*Benzeneazocyanocamphor*, $C_8H_{14}<\begin{matrix}C(CN)\cdot N_2Ph\\ |\\ CO\end{matrix}$, is obtained by adding a solution of cyanocamphor in alcoholic potash gradually and with constant agitation to a solution of diazobenzene chloride cooled to 0°. It forms a yellow, viscous product, which afterwards solidifies, and crystallises from ether in small, yellow needles that melt with decomposition at 155°. It is only slightly soluble in ether, rather more soluble in alcohol, and very soluble in cold benzene.

Orthotolueneazocyanocamphor, $C_{10}H_{14}O\cdot(CN)\cdot N_2\cdot C_7H_7$, is obtained in a similar manner, and forms small, yellow needles, which melt with decomposition at 140°. It is more soluble in ether than its lower homologue, and is very soluble in cold benzene.

Paratolueneazocyanocamphor is obtained in a similar manner, and has similar properties. It melts at 137°, and in solubility is intermediate between the two preceding compounds.

When these derivatives are boiled with alcoholic potash for a few minutes, and the liquid is diluted and acidified with sulphuric acid,

a bulky precipitate separates. If it should at first be gelatinous, it is redissolved in sodium carbonate solution, and reprecipitated with sulphuric acid. When dried in a vacuum over sulphuric acid, they are all light, yellowish bodies, very soluble in cold ether, alcohol, and benzene, from which, however, they cannot be crystallised.

The azobenzene derivative has the empirical formula $C_{20}H_{15}O_3N_3$, and is a monobasic acid; its sodium salt separates from alcohol in yellowish, nacreous plates, and its silver salt rapidly becomes brown when exposed to light. C. H. B.

Alkylcyanocamphors and Alkyl Benzeneazocamphocarboxylates. By A. Haller (*Compt. rend.*, **115**, 97—100).—Methyl methylcamphocarboxylate, when heated with hydrochloric acid, does not decompose even at 150°, but the cyanoalkylcamphors, in contact with hydrochloric acid, decompose to a considerable extent even in the cold, yielding cyanocamphor and alkyl chlorides. If the mixture is heated, camphocarboxylic acid is formed, and this in its turn yields camphor and carbonic anhydride.

Alcoholic solution of hydrogen chloride acts in the same way as the aqueous acid, and sulphuric acid acts even more rapidly than hydrochloric acid, the products being cyanocamphor and probably alkyl sulphates.

It seems necessary therefore to assume that the constitution of the alkyl cyanocamphors is represented by one of the following formulæ:—

$$(1.)\ C_8H_{14}\begin{cases}C{:}CNR\\ |\\ CO\end{cases}. \qquad (2.)\ C_8H_{14}\begin{cases}C{\cdot}CN\\ ||\\ C{\cdot}OR\end{cases}.$$

It would seem that cyanocamphor is tautomeric, and the radicle substituted for the hydrogen attaches itself to either the cyanogen group or the CO group, according to its nature.

Minguin has shown (preceding abstract) that the alkyl camphocarboxylates react with diazochlorides, and yield azo-derivatives.

Methyl benzeneazocamphocarboxylate, $\begin{matrix}C_8H_{14}\\ |\\ CO\end{matrix}\!>\!C\!<\!\begin{matrix}N_2{\cdot}C_6H_5\\ COOMe\end{matrix}$, is obtained by the action of diazobenzene chloride on methyl camphocarboxylate previously mixed with a solution of sodium in methyl alcohol. It separates as a viscous precipitate, which is dissolved in ether, and the ether is evaporated, when the residue gradually solidifies.

It crystallises from alcohol in beautiful, brilliant, yellow crystals, soluble in alcohol, ether, benzene, or toluene, less soluble in light petroleum, insoluble in alkalis. The crystals melt at 78°. When boiled with alcoholic potash, an acid is obtained which does not crystallise distinctly, and is very difficult to obtain pure. Hydrochloric and sulphuric acids yield yellow, uncrystallisable products.

Ethyl benzeneazocamphocarboxylate is obtained in a similar manner. It melts at 65·5°, and resembles the methyl salt in its general properties. C. H. B.

Action of Potassium Hypobromite on the Amide of Campholic Acid. By G. Errera (*Gazzetta*, **22**, i, 205—226).—*Campholic acid*, $C_9H_{17}\cdot COOH$, is best prepared by heating a solution of camphor (500 grams) in benzene (250 grams) in an iron cylinder to the boiling point, gradually adding metallic sodium (38 grams), distilling off the benzene at 180°, and heating the residual mass at 280° for 24 hours. The brown, viscous product is treated with hot water, shaken with ether, and the aqueous liquid acidified with hydrochloric acid and distilled. The yield is about 20 per cent. of pure acid. The *amide*, $C_9H_{17}\cdot CONH_2$, is prepared by heating the acid chloride with aqueous ammonia. It is separated from a small quantity of nitrile, which accompanies it, by distilling the mixture with water, the nitrile passing over with the steam. The amide crystallises from light petroleum in colourless, brilliant prisms, melts at 79—80°, dissolves readily in boiling water, separating from the solution, on cooling, in long, silky needles; it is freely soluble in alcohol and benzene. It strongly resists the action of bases, and is only converted into the acid with difficulty by prolonged boiling with potash. The change is readily effected, however, by heating it with dilute hydrochloric acid in a closed tube at 180°. On heating it with phosphoric anhydride, it yields the corresponding nitrile.

The *nitrile*, $C_9H_{17}\cdot CN$, is a colourless solid resembling camphor in appearance and odour, it melts at 72—73°, boils at 217—219°, and volatilises in a current of steam. It is insoluble in water, but very freely soluble in other solvents. It powerfully resists the action of bases, but is converted into campholic acid under the same conditions as the amide. When heated in alkaline solution at 40° with hydrogen peroxide, it is very partially converted into the amide. On reducing it with sodium in alcoholic solution, the corresponding amine, *campholamine*, $C_9H_{17}\cdot CH_2\cdot NH_2$, is obtained.

Campholyl isocyanate is prepared by dissolving campholamide in bromine (1 mol.), adding a 10 per cent. solution of potash until the liquid is decolorised, and repeatedly distilling in steam. It is a light, colourless liquid, which has the characteristic properties of the isocyanates, with the exception of the odour.

Bicampholylcarbamide, $CO(NH\cdot C_9H_{17})_2$.—This is the composition of the non-volatile residue, obtained in the preparation of the preceding compound; it may also be prepared by treating that substance with potash. It crystallises from alcohol in long, brilliant, flattened needles containing 1 mol. of alcohol, which they lose on exposure to the air, becoming dull and opaque. It melts at 220—221° and readily sublimes, boiling with decomposition at a slightly higher temperature. It is insoluble in water, but freely soluble in hot benzene. When heated in a closed tube at 150° with dilute hydrochloric acid, the product is a substance free from nitrogen. On heating it with water at 200°, the product probably consists of campholylamine.

Monocampholylcarbamide, $NH_2\cdot CO\cdot NH\cdot C_9H_{17}$, prepared by the action of ammonia on campholyl isocyanate, crystallises from water and light petroleum in long, thin needles, melts at 116—117°, and dissolves freely in alcohol and benzene, but only sparingly in cold water or light petroleum.

Campholylamine, $C_9H_{17}\cdot NH_2$.—On passing a current of hydrogen chloride through a mixture of campholyl isocyanate with a little light petroleum, a mass of crystals of an unstable additive compound separates; on adding water and gently heating, an energetic reaction takes place, the crystals disappear, and the liquid separates into two layers, of which the lower contains campholylamine hydrochloride. The free base is a colourless, waxy solid, resembling camphor in appearance, and having an ammoniacal and alliaceous odour; it boils at 174°, and has powerful basic properties. Its *hydrochloride* crystallises in large tabular prisms, very soluble in water. S. B. A. A.

Note.—The author applies the term "campholyl," to the radicle of the series containing 9 carbon atoms, next below and homologous with the campholic series.

Function of Camphoric Acid. By A. Haller (*Compt. rend.*, **114**, 1516—1520).—The action of hydrogen chloride on a solution of camphoric acid in methyl alcohol yields a mixture of methyl camphorates in proportions which vary with the conditions. *Methyl hydrogen camphorate* crystallises from a mixture of ether and light petroleum in large crystals, frequently lozenge-shaped, soluble in alcohol, benzene, toluene, and light petroleum, also in alkali hydroxides and carbonates. *Methyl camphorate* is a thick, oily liquid, which boils at 146—150° under a pressure of 10 mm., and at 175° under a pressure of 65 mm. It can also be prepared by heating in sealed tubes at 100° a mixture of methyl hydrogen camphorate, sodium methoxide, and methyl iodide. When treated with an equivalent quantity of alcoholic potash, it yields the potassium salt of the methyl hydrogen camphorate of saponification. The methyl hydrogen camphorate obtained by direct etherification seems to differ from that obtained by saponification. Their melting points and rotatory powers are as follows:—

	Melting point.	Specific rotatory power.
Methyl hydrogen camphorate of etherification	75—76°	$[\alpha]_D = +51{\cdot}52°$
Methyl hydrogen camphorate of saponification.....	85—86°	$[\alpha]_D = +43{\cdot}55°$
Methyl camphorate		$[\alpha]_D = +44{\cdot}40°$

All these ethereal salts on saponification yield camphoric acid.

When methyl hydrogen camphorate obtained by etherification is heated with phenylhydrazine in sealed tubes at 150—160°, it yields a compound which crystallises from a mixture of ether and light petroleum, and is purified by crystallisation; this melts at 119°, has a molecular rotatory power $[\alpha]_D = +16{\cdot}41°$, and has the composition of a pyrazolone corresponding with camphoric acid. It has, however, none of the properties of the pyrazolones, is insoluble in alkalis, and gives no coloration with ferric chloride. In function and constitution, it is analogous to the phthalylphenylhydrazine and succinylphenylhydrazine obtained by Hötte by the action of phthalic and succinic anhydrides respectively on phenylhydrazine. It would seem, therefore, that camphoric acid is dicarboxylic, and has the constitution $C_8H_{14}(COOH)_2$. This

view is supported by the fact that the compound in question can be obtained by the direct action of camphoric anhydride on phenylhydrazine (Friedel and Combes). Methyl camphorate has no action on phenylhydrazine at 100°, and, although there is an action at 150—160°, no definite products were isolated.

Methyl hydrogen camphorate, when gently heated with benzoic chloride, yields benzoic acid and camphoric anhydride, and in this respect behaves like camphoric acid. Methyl hydrogen camphorate, when dissolved in sodium hydroxide and treated with excess of benzoic chloride, yields a highly refractive liquid, which has the composition $C_{18}H_{22}O_4$, boils at 270—315° under a pressure of 80 mm., and is insoluble in alkalis. C. H. B.

Constitution of Camphoric Acid. By A. Haller (*Compt. rend.*, **115**, 19—21; compare preceding abstract).—When methyl hydrogen camphorate, obtained by etherification, is heated with a molecular proportion of phenylcarbimide at a temperature not exceeding 100°, it yields carbonic anhydride, diphenylcarbamide, and a product which dissolves in a mixture of ether and light petroleum, and crystallises in slender, white needles, soluble in alcohol, ether, benzene, and toluene, but insoluble in water or in alkalis. It melts at 78—79°, and its molecular rotatory power is $[\alpha]_D = +49° 20'$. It has the composition $C_{22}H_{34}O_7$, and its molecular weight, as determined by Raoult's method, in acetic acid solution, is 410. It seems, therefore, that no urethane is formed, and the phenylcarbimide acts simply as a dehydrating agent. It is noteworthy that methyl hydrogen phthalate and methyl hydrogen succinate, when heated with phenylcarbimide, yield phthalimide and succinimide respectively.

Methyl hydrogen camphorate, obtained by saponification (*loc. cit.*), when heated with phenylcarbimide under similar conditions, also yields a compound $C_{22}H_{31}O_7$, which crystallises from light petroleum in a radiated mass, and from alcohol in radiating groups of needles. It is soluble in ether and benzene, less soluble in light petroleum, insoluble in cold alkalis, melts at 62°, and has a molecular rotatory power $[\alpha]_D = +81° 27'$. The other products are carbonic anhydride and diphenylcarbamide, and it follows that the general nature of the reaction is the same as with methyl hydrogen camphorate obtained by etherification. It is impossible, therefore, to assume that the two isomerides have different functions. C. H. B.

Essential Oils. By Schimmel (*Zeit. anal. Chem.*, **31**, 357—358). —*Oil of Lavender.*—The true oil contains no camphor, and but traces of substances of low boiling point. Cineole, which occurs in considerable proportions in oil of *Lavandula spica*, is likewise absent from the true oil, the chief constituents of which are an alcohol, $C_{10}H_{18}O$, identical with Semmler's linaloöl (Abstr., 1891, 540), and its acetate. The alcohol boils at 197—199°, has a sp. gr. of 0·869 at 20°, and in a 100-mm. tube rotates the plane of polarised light through −10° 35'; the refractive index for D is 1·64. [In another part of the paper the sp. gr. of pure linaloöl is stated to be 0·878 at 15°, and its optical rotating power as +2°.] Heated with dehydrating agents, it

yields dipentene and terpinene, also other products. On oxidation, it yields geranaldehyde ("citral"), whose sp. gr. is 0·8972 (Abstr., 1891, 539, where it is misprinted 0·1972); refractive index 1·490. Geranaldehyde is converted by dehydrating agents into cymene. Linaloöl absorbs 4 atoms of bromine; with hydrogen chloride it yields a liquid of the composition $C_{10}H_{18}Cl_2$. Acid anhydrides produce the corresponding ethers, which are substances of agreeable odour. The acetate occurs to the extent of 40 per cent. in oil of bergamot, and has the characteristic odour of that oil.

Thoms' method of valuing oil of cloves (this vol., p. 250) affords results agreeing within 1 per cent. On the other hand, Panajotow's proposal for the detection of geranium oil in oil of rose, by means of a magenta solution decolorised by sulphurous acid, is useless.

M. J. S.

Isomerism in the Limonene Series. By O. Wallach (*Annalen*, **270**, 171—196).—*Benzoyllimonene nitrosochloride*, $C_{17}H_{20}NO_2Cl$, is slowly formed when α-limonene nitrosochloride is treated with benzoic chloride in ethereal solution at the ordinary temperature; it separates from ethyl acetate in rhombic crystals, and is only sparingly soluble in ether. This compound exists in two optically active modifications, corresponding with the two α-limonene nitrosochlorides; both forms melt at 109—110°, and have a specific rotatory power $[\alpha]_D = \pm 101{\cdot}8°$. When equal quantities of the dextrorotatory and lævorotatory compounds are dissolved in ethyl acetate, the inactive *dipentene* derivative is deposited in crystals on evaporating; this substance melts at 90°, and is much more readily soluble than the two active modifications.

β-Limonene nitrosochloride yields a benzoyl derivative, which is identical with that obtained from the α-compound.

Benzoylhydrochlorocarvoxime, $C_{17}H_{20}NO_2Cl$ (m. p. 114—115°), prepared from dextrorotatory hydrochlorocarvoxime, has a specific rotatory power $[\alpha]_D = -10{\cdot}58°$; the benzoyl derivative of the corresponding lævorotatory compound has a specific rotatory power $[\alpha]_D = 9{\cdot}92°$; it is evident, therefore, that these compounds are not identical, but isomeric with the benzoyl derivatives of the limonene nitrosochlorides.

The two limonenenitrolanilides prepared from α-limonene nitrosochloride are identical in properties with the corresponding compounds obtained from β-limonene nitrosochloride.

α-Limonenenitrolanilide forms monosymmetric crystals, melts at 112—113°, and exists in two modifications having specific rotatory powers $[\alpha]_D = \pm 101{\cdot}75°$ to $102{\cdot}62°$. The *nitroso*-derivative,

$$NO{\cdot}C_{10}H_{16}{\cdot}NPh{\cdot}NO,$$

prepared by treating α-limonenenitrolanilide with sodium nitrite and acetic acid, separates from hot alcohol in colourless crystals, melts at 142°, and is soluble in about 10 parts of ether or benzene, but only sparingly in cold glacial acetic acid; it exists in two optically active modifications, $[\alpha]_D = \pm 46{\cdot}20°$ to $47{\cdot}82°$, corresponding with the two optically active α-nitrolanilides, and by combining equal quantities of the two substances *α-nitrosodipentenenitrolanilide* is obtained in well-defined crystals, which melt at 147° with decomposition.

β-Limonenenitrolanilide crystallises in moss-like needles, melts at 153°, and is readily soluble in chloroform, alcohol, and hot benzene, but only sparingly in ether, and insoluble in light petroleum; its specific rotatory power is $[\alpha]_D = \pm 87{\cdot}17°$ to 89·39°. The *nitroso*-derivative separates from hot alcohol in yellowish prisms, and melts at 136° with decomposition; it exists in two optically active modifications which when combined form an inactive compound melting at 129°.

The above experiments seem to prove that α- and β-limonene nitrosochloride are chemically identical, but whether this is true or not in the case of the α- and β-nitrolanilides is an open question. In the first place, it has not yet been found possible to convert one nitrolanilide into the other; the basicity of the two compounds is widely different, the α-anilide being precipitated from its solution in acetic acid on the addition of water, whilst the β-compound remains in solution in the form of its acetate. Both compounds undergo decomposition on heating; the α-anilide yields aniline and carvoxime, whereas the β-compound gives aniline and a substance which has a distinct isonitrile-like odour. When dextrorotatory α-limonenenitrolanilide is treated with hydrogen chloride in methyl alcoholic solution and, after keeping for some days, the solvent is evaporated, a crystalline powder is left; this, after having been washed with ammonia and recrystallised from alcohol, melts at 115°, and is very similar to hydrochlorolimonenenitrolanilide (see below) in appearance. Both dextrorotatory and lævorotatory β-limonenenitrolanilide give under the same conditions a crystalline substance of the composition $C_{16}H_{23}ClN_2O$, which melts at 78°; the inactive dipentene derivative, obtained by combining these two active modifications (m. p. 78°), melts at 90°. The α- and β-nitrolanilides were proved to have the same molecular weight by determinations carried out by the boiling point method.

Hydrochlorolimonene does not combine with anhydrous hydrogen chloride; when kept for some time, it seems to undergo polymerisation and, at the same time, its rotatory power diminishes.

Hydrochlorolimonenenitrolbenzylamine, $NO{\cdot}C_{10}H_{17}Cl{\cdot}NH{\cdot}C_7H_7$, prepared by treating the dextrorotatory nitrosate with benzylamine in alcoholic solution, crystallises in moss-like needles, melts at 103—104°, and is very readily soluble in alcohol, ether, and benzene, but only sparingly in cold, light petroleum; its specific rotatory power is $[\alpha]_D = +149{\cdot}6°$. When treated with hydrogen chloride in ethereal solution, it yields a crystalline salt, which melts at 163—164°, and is dextrorotatory. The corresponding lævorotatory compound, prepared in like manner, has a specific rotatory power $[\alpha]_D = -147{\cdot}4°$.

Hydrochlorodipentenenitrolbenzylamine is invariably obtained as a bye-product in the preparation of the active isomerides; it is but sparingly soluble in all solvents, and melts at 150°.

Hydrochlorolimonenenitrolanilide, $NO{\cdot}C_{10}H_{17}Cl{\cdot}NHPh$, is formed, together with the corresponding dipentene derivative, when aniline is added to a warm benzene solution of the nitrosate; it separates from alcohol in crystals, melts at 117—118°, and is optically active in the same direction as the nitrosate from which it has been prepared.

The corresponding *dipentene* derivative melts at 139—141°, and is much more sparingly soluble in alcohol; when treated with alcoholic potash, it yields two bases, melting at 123—124° and 158° respectively, which closely resemble the α- and β-nitrolanilides of the dipentene series. F. S. K.

Constitution of Carvene. By A. Reychler (*Bull. Soc. Chim.* [3], **7**, 36—41).—A theoretical discussion as to the constitution of carvene and of limonene. T. G. N.

Action of Chlorine on Dihydrochlorodipentene. By O. Wallach and A. Hesse (*Annalen*, **270**, 196—203).—A *trichloride*, of the composition $C_{10}H_{17}Cl_3$, is formed, with evolution of hydrogen chloride, when well-dried chlorine is passed into a carbon bisulphide solution of dihydrochlorodipentene exposed to direct sunlight, until the colour, which first becomes green, has changed to yellow; it crystallises from alcohol in lustrous, colourless plates, melts at 87°, and boils at 145—150° under a pressure of 10 mm. The *tetrachloride*, $C_{10}H_{16}Cl_4$, is obtained when the treatment with chlorine is continued, under the conditions just described, for a long time; after purification by fractional distillation under reduced pressure, the product separates from ethyl acetate in well-defined symmetric crystals, melting at 108°.

When the trichloride is warmed for 6—7 hours with excess of sodium ethoxide in alcoholic solution, it yields a heavy oil, which still contains chlorine; when boiled for 5—6 hours with a glacial acetic acid solution of sodium acetate, it is converted into an oily *dichloride* of the composition $C_{10}H_{16}Cl_2$. This dichloride combines with hydrogen chloride in glacial acetic acid solution, yielding the original trichloride; when treated with bromine in glacial acetic acid solution, it yields a *dibromide* of the composition $C_{10}H_{16}Cl_2Br_2$, which, on recrystallisation from ethyl acetate, is deposited in transparent prisms melting at 98°.

The *nitrosochloride*, $C_{10}H_{16}Cl_2,NOCl$, prepared by treating the dichloride with amyl nitrite and hydrochloric acid in glacial acetic acid solution, is a crystalline powder melting at 111°. The *nitrolanilide*, $NO{\cdot}C_{10}H_{16}Cl_2{\cdot}NHPh$, crystallises in slender needles, and melts at 140—141°. The *nitrolpiperidide*, $NO{\cdot}C_{10}H_{16}Cl_2{\cdot}C_5NH_{10}$, crystallises from alcohol in lustrous plates, and melts at 147°. F. S. K.

Degree of Saturation of the Dextroterpene from Russian Turpentine. By A. Shtchoukareff (*J. Russ. Chem. Soc.*, **22**, 290—296).—The author has made an investigation on the number of atoms of bromine which a molecule of the right-handed terpene from Russian turpentine can directly take up. His first method was to dissolve a known quantity of the turpentine in chloroform (afterwards discarded for carbon tetrachloride), and add to this solution, in a stoppered flask, bromine solution of known strength (also in chloroform or carbon tetrachloride), until the colour ceased to disappear after 5 or 10 minutes. The contents of the flask were then shaken up with water, and the aqueous solution titrated with standard alkali,

to ascertain the quantity of hydrobromic acid formed, if any. The following table gives specimens of his results :—

Experiment.	I.	II.	III.
Bromine required by 1 mol. (136 parts) $C_{10}H_{16}$	169	151	172
Bromine converted into HBr	18	21	21

His second method was to add, at once, a large excess of bromine, allow the mixture to remain for a considerable time, titrate the unchanged bromine by means of potassium iodide and sodium thiosulphate, and titrate for hydrobromic acid with standard potash solution.

A considerably larger quantity of bromine disappeared under these conditions, as may be seen from the following table :—

Experiment.	I.	II.	III.
Bromine required by 1 mol. $C_{10}H_{16}$	307	317	309
Bromine converted into HBr	54	52	47

These last results confirm Tilden's observations on the pinenes, which take up more than 2 atoms of bromine per molecule. The author considers that the terpene examined, when treated with excess of bromine, combines with 4 atoms of the halogen to form an unstable compound $C_{10}H_{16}Br_4$, which decomposes in part into $C_{10}H_{15}Br_3$ and hydrogen bromide. This is analogous to the behaviour of the camphenes, which absorb 2 atoms of bromine, and then give off 1 mol. of hydrogen bromide. J. W.

Reduction of Hydrate of Terpinol. By A. Shtchoukareff (*J. Russ. Chem. Soc.*, 22, 296—298). — Hydrate of terpinol, $C_{10}H_{20}O_2 + H_2O$, heated at 210° in a sealed tube with 1½ times the theoretical quantity of hydriodic acid of sp. gr. 1·7, and a little amorphous phosphorus, yields a large quantity of a hydrocarbon, $C_{10}H_{20}$. A portion of the crude reduction product is volatile with steam, boiling at 165—172°. This portion was treated with fuming sulphuric acid, washed, boiled some hours with metallic sodium, and fractionated; about half passed over between 168° and 170°. This is the hydrocarbon $C_{10}H_{20}$. Its sp. gr. at 15°/15° is 0·797. It is not attacked by sulphuric acid or by bromine at the ordinary temperature, and does not form a crystalline product with bromine in presence of aluminium bromide. It is probably identical with the hydrocarbon of the same composition obtained from menthol.

The portion not volatile with steam (more than half of the whole reduced product) boiled mostly between 310° and 315°. It is a viscous, fluorescent liquid. J. W.

Condurangin. By G. Carrara (*Gazzetta*, **22**, i, 236—242).—Condurangin is a glucoside, first obtained by Vulpius, from the bark of *Gonolobus condurango*, and considered by some writers as identical with vincetoxin from *Asclepias vincetoxicum*. It may be separated into two parts, one of which is soluble in water, the other insoluble. The best method of preparing it, is to extract the bark with 95 per cent. alcohol in a reflux apparatus, filter, distil off the greater part of the alcohol, take up with cold water, filter again, add concentrated solution of ammonium carbonate, and heat gently. The precipitate thus formed is washed with hot water, redissolved in cold water, containing, if necessary, a few drops of alcohol, basic lead acetate added, the precipitate thoroughly washed, suspended in water, and decomposed with hydrogen sulphide; the brown solution obtained is then precipitated with a concentrated solution of common salt. The precipitate, after purification, consists of a mixture of the two modifications of condurangin. Insoluble condurangin is precipitated from a benzene solution on the addition of excess of light petroleum, as a light, almost white powder, which melts at 60—61°, and has the percentage composition $C_{20}H_{32}O_6$. Its molecular weight, as determined by the cryoscopic method, agrees with this formula.

Soluble condurangin, obtained by the evaporation of an aqueous extract of the mixed varieties, is a yellowish substance melting at 134°. It appears to have the composition $C_{18}H_{28}O_7$, but its molecular weight could not be determined. On boiling either of these compounds with acids, the principal product is a brown, pitchy substance, insoluble in water. With Fröhde's reagent, an aqueous solution of the soluble condurangin yields a greenish coloration, and after a time a flocculent, green precipitate, the insoluble variety, suspended in water, gives no reaction, or only a yellowish coloration.

S. B. A. A.

Santonic Acid. By L. Francesconi (*Gazzetta*, **22**, i, 181—205).—*Santonic acid*, $C_{15}H_{20}O_4$, was first obtained by Cannizzaro by the action of baryta on santonin, and many of its properties have already been described.

The *oxime* of ethyl santonate, $COOEt{\cdot}C_{12}H_{17}O{<}\begin{matrix}CH_2\\|\\C{:}NOH\end{matrix}$, crystallises from alcohol in tufts of white laminæ, melts at 126—127°, dissolves readily in ether and alcohol, but only very sparingly in water. It is lævorotatory, $[\alpha]_D = -36{\cdot}5$. On treating it with dilute hydrochloric acid, it splits up into ethyl santonate and hydroxylamine. In the preparation of this compound, a small quantity of a secondary product is formed, having approximately the composition of the oxime of santonic acid. It crystallises, however, from alcohol in long needles, melting at 189·5°, and is only very sparingly soluble in ether, and almost insoluble in water. It also forms a barium salt, more soluble than that of the acid oxime.

The *oxime* of santonic acid, $COOH{\cdot}C_{12}H_{17}O{<}\begin{matrix}CH_2\\|\\C{:}NOH\end{matrix}$, is best prepared by heating an alcoholic solution of santonic acid and hydroxylamine hydrochloride with precipitated calcium carbonate. When

pure, it forms small crystals melting at 186—187°, and moderately soluble in ether, alcohol, and hot water. It is lævorotatory, $[\alpha]_D = -64{\cdot}9$. Dilute hydrochloric acid decomposes it into santonic acid and hydroxylamine.

The *amine* of ethyl santonate, $COOEt{\cdot}C_{12}H_{17}O{<}\begin{matrix}CH_2\\ |\\ CH{\cdot}NH_2\end{matrix}$, obtained by reducing a solution of the oxime in alcohol and acetic acid with sodium amalgam, crystallises from ether in hexagonal tables, and melts at 130—141°. It dissolves very sparingly in water, forming a strongly alkaline solution, and is moderately soluble in ether and alcohol. It turns yellow if heated for some time at 100°; its alcoholic solution likewise undergoes alteration on heating. It is dextrorotatory, $[\alpha]_D = +131{\cdot}34$.

Hyposantonic acid, $C_{15}H_{20}O_3$, is prepared by heating an acetic acid solution of the preceding amine with sodium nitrite. The pure acid obtained from the barium salt, crystallises from ether in microscopic needles, and melts at 135—136°.

The *hydrazone* of ethyl santonate, $COOEt{\cdot}C_{12}H_{17}O{<}\begin{matrix}CH_2\\ |\\ C{\cdot}N_2HPh\end{matrix}$, crystallises from alcohol in clear, yellow plates, and melts at 115—116°. It is moderately soluble in cold ether and alcohol, but only very sparingly in cold water; it is decomposed by hot water, and readily altered by exposure to sunlight. Its alcoholic solution is blackened by hydrochloric acid. On reducing it with sodium amalgam, only traces of the amine are formed.

On oxidising santonic acid with potassium permanganate, concentrating the clear solution in a vacuum, acidifying with sulphuric acid, repeatedly extracting with much ether, and evaporating the ethereal solution, a viscous residue is obtained, from which, by recrystallisation from a mixture of ether and chloroform, a white solid, melting at 176°, can be separated. This substance is a tetrabasic acid, having the composition $C_{13}H_{18}O_8$; it is very soluble in water, forming a strongly acid solution; it is moderately soluble in ether and alcohol, and insoluble in chloroform; it dissolves in solutions of alkali carbonates with evolution of carbonic anhydride. It is dextrorotatory, $[\alpha]_D = +28{\cdot}56$. The *silver* salt, $C_{13}H_{14}Ag_4O_8$, forms white flakes.

On heating the acid at its melting point, or, preferably, at 180—181°, it loses 1 mol. H_2O, and the *monanhydride*, $C_{13}H_{16}O_7$, is left; this crystallises from dry ether in white, shining prisms, and melts at 192—193°; it dissolves in absolute alcohol, forming a feebly acid solution. On heating the acid or the monanhydride with acetic anhydride for four hours, distilling off the excess of that reagent and adding excess of dry ether, the *dianhydride*, $C_{13}H_{14}O_6$, is precipitated as a white, crystalline powder, consisting of minute plates or tufts of needles. It melts at 151—152°, and is soluble in acetic anhydride or in hot water, but not in ether. On concentrating the aqueous solution of either of these anhydrides, a viscous mass is left, but no crystals are deposited; when this is dried over sulphuric acid in a vacuum, or heated for some hours at 100°, the product is an acid,

strongly resembling the acid obtained by the oxidation of santonic acid, but differing from it in not crystallising from water or ether, in its greater solubility in a mixture of ether and chloroform, and in losing 1 mol. H_2O at 135—145°. When the oxidation acid is dissolved in acetic anhydride at a gentle heat, and dry ether is immediately added, a deposit of long, colourless needles is formed, consisting of a dianhydride, melting at 134—135°. This is converted into the dianhydride, melting at 151—152°, by heating it at its melting point, and its aqueous solution, on concentration, readily yields the acid melting at 176°, together with small quantities of its isomeride.

S. B. A. A.

Chrysophanic Acid. By V. Grandis (*Chem. Centr.*, 1892, i, 592—593; from *Ann. Chim. Farm.*, **15**, 1—9).—The author has prepared chrysophanic acid from chrysarobin according to the directions given by Liebermann, and finds the melting point to lie between 162° and 187°, although the product was repeatedly crystallised from benzene. The sublimed substance melted at 185—187°, and this melting point was further raised to 190—191° by recrystallisation. In all other respects the specimen appeared to be identical with that described by Liebermann. The results of the elementary analysis agreed with the formula $C_{15}H_{10}O_4$, and the diacetyl and dibenzoyl derivatives likewise possessed the melting points and physical characters of the corresponding compounds described by him. J. W. L.

Euxanthic Acid and Euxanthone. By J. Herzig (*Monatsh.*, **13**, 411—421).—In a previous paper, the author has shown that a similiarity exists between euxanthone and quercetin, inasmuch as both yield yellow alkyl derivatives which are insoluble in alkali, and yield colourless compounds on acetylation (Abstr., 1891, 1349). Euxanthic acid on acetylation is also converted into a colourless *tetracetyl* derivative, $C_{13}H_6(OAc)_4O$, which crystallises from alcohol in white plates, and melts at 118—119° (uncorr.). The hydrolysis with sulphuric acid does not proceed so smoothly as with the acetyl derivatives of quercetin and euxanthone, the euxanthic acid being mostly converted into euxanthone by further loss of water, and the filtrate has always a yellow colour.

On alkylation, euxanthic acid no longer behaves in a similar manner to euxanthone, as only the tetrethyl ether, $C_{13}H_6O(OEt)_4$, could be isolated, although small quantities of a yellow substance are formed which may possibly be a lower ether. The tetrethyl ether is sparingly soluble in alcohol, and crystallises from the solution in white plates or flat needles melting at 93—95°. Fisetin, which is closely related to quercetin, resembles euxanthic acid in only yielding the completely ethylated compound.

The tetrethyl ether corresponds with euxanthone in its behaviour towards potash, as it is not attacked by the alcoholic solution at 100°, and even at 150° it is not converted into a phenol and a hydroxy-acid; in this respect, therefore, the euxanthone derivatives differ from those of quercetin, as the latter are readily resolved by potash.

Although euxanthone and xanthone do not combine with hydroxyl-

amine, euxanthic acid readily unites with both. In the case of hydroxylamine, however, the product has the composition $C_{13}H_9NO_4$, the elements of water having been eliminated and a derivative of euxanthone apparently formed; it crystallises in white needles and melts at 233—235°, previously becoming slightly brown. The phenylhydrazone has not been obtained pure.

The following results have also been obtained with regard to the monethyleuxanthones previously described (*loc. cit.*). Both can be obtained from euxanthone and reconverted into it, so that they are true derivatives. The white modification yields an acetyl derivative which crystallises from alcohol in white needles and melts at 164—166°. Neither modification combines with phenylhydrazine.

H. G. C.

Chlorophyll. By N. Monteverde (*Ann. Agron.*, **18**, 268—270).—The author discusses the question of how many different pigments are contained in an alcoholic solution of chlorophyll. If, after Frémy, the alcoholic extract of leaves of wheat be treated with baryta water, and the precipitate exhausted with alcohol, a yellow solution is obtained; on adding some drops of water and shaking with light petroleum, the yellow is separated, and can be purified by agitation with fresh portions of alcohol or light petroleum, the latter dissolving carotin, and the former xanthophyll. The solution of carotin agrees exactly, optically and chemically, with that of crystallisable carotin extracted from carrots or dead leaves; its spectrum shows three absorption bands between F and H. The crystals of xanthophyll are distinguished from those of carotin by their form, colour, and by microchemical reactions, as to which the author entirely confirms Borodin. Whilst hydrochloric acid precipitates carotin from its alcoholic solution without alteration, it decomposes xanthophyll, giving rise to a blue substance, and the three absorption bands between F and H are replaced by continuous absorption at that end of the spectrum. Etiolated leaves of wheat contain only very small quantities of carotin, but after a short daily exposure to light crystallisable carotin can be obtained from them. The author has found these two colouring matters in the yellow autumnal leaves of many ligneous plants. He has extracted from the leaves of *Scrophularia nodosa* a third pigment, agreeing with the "golden yellow," of Borodin. The young leaves of *Potamogeton natans* are yellow-brown, the colour cells containing, in addition to the yellow and green pigments, a red one which disappears later on. This substance is not crystallisable, is insoluble in water, but dissolves easily in alcohol to a cherry-red.

When an alcoholic solution of chlorophyll is shaken with benzene or light petroleum, the upper layer contains both green colouring matter and carotin. If this is decanted, mixed with a large quantity of absolute alcohol, and water added drop by drop, a point can be hit at which all the green colouring matter is transferred to the alcohol, the other solvent retaining the carotin. (The slightest excess of water causes all the green pigment to leave the alcohol.) By repeating this process several times, each time decanting off the solution of carotin, the author obtains a purified green pigment, which gives

only the first four absorption bands and a continuous absorption in the extreme violet. The cyanophyll spectrum of Kraus is, therefore, a combined spectrum of the pure green pigment and carotin. The pure green pigment does not crystallise. Heated with hydrochloric acid, it yields pure brown-yellow chlorophyllane with absorption bands I, IV*a*, IV*b*, II, III, and an absorption in the extreme violet; flocks of pure phyllocyanin are also formed.

The alcoholic extract of certain plants does not behave as above described; the benzene or light petroleum may take only the carotin, leaving the green pigment and xanthophyll in the alcohol. In this case the author speaks of an "inferior green pigment," yielding with hydrochloric acid "inferior chlorophyllane" and "inferior phyllocyanin." This inferior green pigment crystallises in tetrahedra, hexagonal plates, and stars, but oftenest in a very irregular manner. The pure crystals, appearing to the eye as a dark-brown, almost black, powder, are identical with the chlorophyll crystals which Borodin obtained by moistening microscopic sections with alcohol and allowing them to dry. They are easily soluble in alcohol, insoluble in light petroleum, carbon bisulphide, and commercial benzene, but soluble in pure benzene (this explains the contradiction between Tschirch and Borodin). The alcoholic solution is fluorescent; its spectrum has absorption bands I to IV, and possibly bands between F and H. The band IV*b* is entirely absent, from which one must conclude that chlorophyllane is not present, as Tschirch believed.

The author concludes that living leaves contain only the inferior green pigment. Treatment of the leaves with boiling water, however, nearly always transforms the inferior green into the superior. This transformation can only be effected in the leaves themselves, for the crystals of inferior green pigment do not yield the superior when boiled in alcoholic solution. J. M. H. M.

Chloriodides of Organic Bases. By A. Pictet and G. Krafft (*Bull. Soc. Chim.* [3], **7**, 72—75).—When a mixture of iodine trichloride with pyridine, piperidine, quinoline, or trimethylamine, in molecular proportion, is heated with water and the solution concentrated, an abundant crystallisation of yellow needles of the chloriodide of the base is obtained according to the equations:—

$$2ICl_3 + 3H_2O = ICl + 5HCl + HIO_3,$$
$$C_5H_5N + ICl + HCl = C_5H_5N,ICl,HCl,$$

and these salts are identical with those obtained by Ostermayer and by Dittmar (Abstr., 1886, 158).

On treating these salts with sodium hydroxide, the white chloriodides are obtained which are insoluble in water but crystallise from ether in fine needles. They are strongly basic, the primitive salt being regenerated on treating them with hydrochloric acid. The hydrochloride yields double salts with platinum, gold, and mercury chlorides, and the chloriodide also forms crystalline salts with sulphuric, nitric, chromic, and picric acids.

Pyridine chloriodide, C_5H_6N,ICl.—White needles, melting at 132°.

The hydrochloride, C_5H_5N,ICl,HCl, melts at 180° and crystallises from water in long, yellow needles.

Quinoline chloriodide, C_9H_7N,ICl.—Small, white needles, melting at 159·5°. The hydrochloride, C_9H_7N,ICl,HCl, melting at 118°, is Osterwald's quinoiodine.

Piperidine chloriodide, $C_5H_{11}N,ICl$.—Fine, white needles, melting at 143°. The hydrochloride, $C_5H_{11}N,ICl,HCl$, forms yellow crystals and melts at 90°.

Trimethylamine chloriodide, NMe_3,ICl.—White needles, melting at 77°. The hydrochloride, NMe_3,ICl,HCl, forms yellow, tabular crystals and melts at 159°. The formation of this salt proves Dittmar's assertion, that the chloriodides are peculiar to the pyridine derivatives, to be incorrect. The authors consider that in the molecule of these chloriodides the nitrogen is pentavalent and is linked to each of the halogen atoms. T. G. N.

Pyridine-like Bases in Petroleum. By R. Zaloziecki (*Monatsh.*, **13**, 498—503).—These were obtained from the petroleum of Boryslav by diluting the acid which had been used to wash the oil, removing the tarry matter thus set free, adding quicklime in excess to the acid liquid, and distilling the bases thus liberated with steam. A mixture of bases was obtained, which exhibited many properties of the pyridine compounds. With platinum tetrachloride, one crystalline substance was obtained, which was probably the platosochloride of a hydrogenised pyridine, such as dihydrocoridine, $(C_5NMe_5H_2Cl)_2,PtCl_2$. The pyridine compounds are products of decomposition of the animal body, and their occurrence in petroleum is important as bearing on the formation of the latter. C. F. B.

Pyridinecarboxylic Acids obtained from Berberine. By R. Mayer (*Monatsh.*, **13**, 344—356).—The author has prepared berberonic acid (pyridinetricarboxylic acid) by the oxidation of commercial berberine (200 grams) with nitric acid, and finds that it melts at 234—235°, some 12 degrees lower than is given by Fürth (*Monatsh.*, **2**, 426). On boiling with a mixture of acetic acid and anhydride for six hours, it is converted, with loss of carbonic anhydride, into beronic acid. The latter agrees in all its properties, except that it melts at 249° instead of 263°, with the compound described by Fürth; and is shown by the crystalline form of its hydrochloride to be identical with cinchomeronic acid ($\beta\gamma$-pyridinedicarboxylic acid). The position of the third carboxyl group in berberonic acid must be either the α- or α_1-, since, with ferrous sulphate, it gives the characteristic blood-red coloration of substances so constituted. $\alpha\beta\gamma$-pyridinecarboxylic acid is known and is not identical with it, so that berberonic acid must be the $\alpha_1\beta\gamma$-compound.

The bye-product, of a yellow colour, obtained by Weidel (*Ber.*, **12**, 1148) during the oxidation of berberine by nitric acid, and thought by him to be a nitro-compound, proves to be merely impure cinchomeronic acid. G. T. M.

Derivatives of 2-Methyl-5-ethylpyridylalkine, $C_9H_{13}NO$. By G. Prausnitz (*Ber.*, **25**, 2394—2397).—*Ethylvinylpyridine*, $C_5NH_4Et{\cdot}CH{:}CH_2$, is obtained by heating methylethylpyridylalkine with 3—4 parts of concentrated hydrochloric acid in a sealed tube at 160—170° for 4—5 hours. The product is saturated with sodium hydroxide and distilled with steam. An oil is obtained which is extracted by shaking with ether, and the ethereal solution dried with potassium carbonate and evaporated. It boils at 98—102° under a pressure of 21 mm., is colourless, has an unpleasant odour, and is very easily soluble in ether, alcohol, and chloroform, sparingly so in water. The same compound is obtained by distilling the alkine over solid potassium hydroxide. The *aurochloride* is an oil. The *platinochloride* is not characteristic. The *double salt* with *mercuric chloride*, $(C_9H_{11}N.HCl)_2,5HgCl_2$, crystallises in beautiful needles, and is insoluble in cold water, sparingly soluble in hot water.

2-*Methyl*-5-*ethylpiperidylalkine*, $C_5NH_9Et{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by gradually adding alcohol (300 grams) to a mixture of metallic sodium (40 grams) and methylethylpyridylalkine (10 grams) dissolved in alcohol. The product is mixed with concentrated hydrochloric acid, the sodium chloride separated, and the filtrate evaporated to dryness and extracted with absolute alcohol. The solution is evaporated to a syrup, mixed with chloroform and concentrated sodium hydroxide, well shaken, and the chloroform extract dried over potassium carbonate and distilled under diminished pressure. First, a compound of the formula $C_{17}H_{35}N_3$ distils over at 105—110° under a pressure of 18 mm.; then methylethylpiperidylalkine distils at 170—180°; this is a viscid, colourless liquid, of strongly alkaline reaction, and is easily soluble in chloroform, less so in alcohol and ether. When treated with sodium nitrite, it yields an oily nitrosamine.

Diethylpiperidine, $C_5NH_9Et_2$, is obtained by reducing the alkine by Ladenburg's or Bamberger's method. After decomposing, by water, the sodium ethoxide which is formed, the alcohol is distilled off, and the residue extracted with ether. The ether is then distilled off, and the residue distilled with steam. The distillate thus obtained is acidified with hydrochloric acid, evaporated to a syrup, and allowed to crystallise over sulphuric acid in a vacuum. The hydrochloride thus obtained rapidly deliquesces on exposure to air. The *base* is obtained by decomposing the hydrochloride with solid potassium hydroxide; it boils at 100—105° under a pressure of 22 mm., and at 190° under the ordinary pressure. It is a colourless, limpid liquid, has a nauseous odour, reacts strongly alkaline to litmus, is very easily soluble in chloroform and ether, and yields an oily nitrosamine. Its sp. gr. = 0·8722 at 0°. E. C. R.

Quaternary Ammonium Bases of the Quinoline Series. By A. Claus (*J. pr. Chem.* [2], **46**, 106—128).—It has been shown (Abstr., 1891, 1252; this vol., p. 876) that two classes of bases are obtainable by the action of potassium hydroxide and of moist silver oxide on the halogen alkyl compounds of substituted quinolines. Those of the one kind are soluble in ether and include the bases prepared by acting with alkalis or moist silver oxide on the alkyl halogen

compounds of quinoline, of halogenised or nitrated quinolines, and, in certain cases (*loc. cit.*), of hydroxyquinolines; the author maintains that these bases are alkylene quinolines. Those of the other kind are insoluble in ether, and result, in most cases, from the action of alkalis or moist silver oxide on halogen alkyl compounds of hydroxyquinolines; these are quaternary ammonium bases. Experiments are quoted to show that Decker's nitrobromoquinolinemethylium hydroxide (this vol., p. 880) is not itself a base soluble in ether, but is converted into one by the combined action of the alkali and ether.

The bases insoluble in ether do not undergo oxidation when exposed to air or to the action of potassium ferricyanide, whereas the bases soluble in ether are oxidised under these circumstances without exception. In close connection with this observation, some experiments on the electrolysis of 3-hydroxyquinoline methosulphate and 4′-bromoquinoline methosulphate are touched on; details of this work will shortly be published. Some remarks on Decker's bases from acridine and phenylacridine (*loc. cit.*) conclude the paper.

A. G. B.

Methylhydroxytoluquinoxaline and the Constitution of the Compounds obtained from α-Hydroxy-acids and Orthodiamines. By O. Hinsberg (*Ber.*, **25**, 2416—2421).—Autenrieth and Hinsberg (this vol., p. 709) came to the conclusion that no quinoxaline derivative is formed from orthotoluylenediamine and mandelic acid. Georgescu (this vol., p. 886). however, states that derivatives of tetraketoquinoxaline are obtained by the action of orthodiamines on mandelic acid and other α-hydroxy-acids. The author has arrived at the constitution of the compounds in the following way. Georgescu obtained a compound, to which he gave the formula

$$C_7H_6<\begin{matrix}NH\cdot CHMe\\ NH\cdot CO\end{matrix},$$

by the action of lactic acid on orthotoluylenediamine at 130°. A compound of this constitution should be obtained by reducing the nitro-compound $NO_2\cdot C_7H_6\cdot NH\cdot CHMe\cdot COOH$, and also by the action of ethyl α-bromopropionate on orthotoluylenediamine. By these methods the author has obtained a quinoxaline derivative of the above constitution which has quite different properties from those of Georgescu's compound.

Nitrotolualanine, $NO_2\cdot C_7H_6\cdot NH\cdot CHMe\cdot COOH$, is obtained by heating nitrotoluidine (2 mols.) with bromopropionic acid (1 mol.) for some hours at 115—120°. The product is warmed with dilute sodium hydroxide, and the yellow solution filtered and freed from nitrotoluidine by shaking with ether. On adding excess of hydrochloric acid to the alkaline liquid thus obtained, the nitrotolualanine is precipitated as an oil which soon solidifies. It crystallises from dilute alcohol in leaflets, melts at 148°, is sparingly soluble in water, easily so in ether and alcohol, and yields intensely reddish-yellow solutions.

Metamethyl-α-oxy-β-methylhydroquinoxaline, $C_6H_3<\begin{matrix}NH\cdot CHMe\\ NH\cdot CO\end{matrix}$, is

obtained by reducing the preceding nitro-compound with tin and hydrochloric acid. The greater part of the reduction product crystallises out as stannochloride; this is dissolved in hot water and alcohol, decomposed with excess of ammonia, and the precipitated hydroxymethyltoluquinoxaline purified by crystallisation from dilute alcohol. It is thus obtained in white leaflets, melts at 157°, is sparingly soluble in cold water, easily so in alcohol and ether. It is slightly decomposed on exposure to air, yields colourless solutions with dilute mineral acids, and dissolves in warm potassium and sodium hydroxides. When treated with sodium nitrite, in dilute acid solution, the *nitrosamine* is obtained in voluminous, slender, white needles which dissolve in alkalis with a yellowish-red colour. When oxidised with iodine and soda solution, or with silver nitrate and ammonia, it is easily converted into methylhydroxytoluquinoxaline which melts at 257°.

Hydromethyloxytoluquinoxaline is also obtained by heating pure toluylenediamine (3 mols.) and ethyl bromopropionate (2 mols.) for half an hour on the water bath in a current of carbonic anhydride. The product is dissolved in water, extracted with ether, the ethereal solution evaporated to dryness, and the residue crystallised first from water and then from dilute alcohol. The product obtained melted at 148—151°, but otherwise had the same properties as that obtained by the first method. The author believes that the impurity in this preparation is paramethyl-α-oxy-β-methylhydroquinoxaline.

E. C. R.

Action of Benzaldehyde on 2 : 6-Lutidine. By F. Schuster (*Ber.*, **25**, 2398—2405).—Benzylidene-2 : 6-lutidine and dibenzylidene-2 : 6-lutidine are obtained by the action of benzaldehyde on 2 : 6-lutidine. A mixture of benzaldehyde with 2 : 6-lutidine is heated with zinc chloride in a sealed tube at 225° for six hours; the product, a white, crystalline mass mixed with a small quantity of brown resin, is easily purified by drying on porous plates. The two bases thus obtained are separated by means of their hydrochlorides, benzylidene-2 : 6-lutidine hydrochloride being easily soluble in water, whilst the hydrochloride of the dibenzylidene base is very sparingly soluble. The hydrochlorides are easily decomposed by potassium hydroxide, the latter salt more easily on heating; a large excess of alkali is to be avoided, as the bases are somewhat soluble in alkali. The author was unable to obtain an intermediate compound of the aldol series by heating the components without the addition of zinc chloride; the monobenzylidene base cannot be obtained alone, but is always produced together with the dibenzylidene base.

Benzylidene-2 : 6-lutidine, $C_5NH_3Me{\cdot}CH{:}CHPh$, crystallises out in beautiful, nacreous plates when water is added to the alcoholic solution until a slight turbidity is produced. It melts at 123°, has a faint, characteristic odour, is easily soluble in ether, alcohol, benzene, chloroform, and carbon bisulphide, is volatile with difficulty in a current of steam, and is neutral to litmus. The *hydrochloride* crystallises in very slender, pale-yellow needles, and melts at 50°; when recrystallised from hydrochloric acid, it forms beautiful, bright-yellow crystals which contain 1 mol. H_2O. The anhydrous salt is

colourless, turns brown at 200°, and melts at 221° with decomposition. The *chromate* crystallises in yellowish-red needles, is easily soluble in boiling water, sparingly so in the cold, and turns brown at 280° without melting. The *mercurochloride*, $C_{14}NH_{13},HHgCl_3$, crystallises in interlacing needles, melts at 185°, and is sparingly soluble in cold water, but easily in alcohol and boiling water. The *platinochloride* crystallises in reddish-yellow, sparingly soluble needles, and blackens at 270°, but does not melt. The *aurochloride* crystallises in brick-red needles, melts at 211°, and is sparingly soluble in alcohol, almost insoluble in boiling water. The *picrate* crystallises in golden spangles, coagulates, blackens on heating, and melts at 217—219° with decomposition. The base also yields a sparingly soluble double salt with potassium ferrocyanide. The *hydrobromide* and *iodide* crystallise in sparingly soluble needles.

A *dibromide* of the formula $C_5NH_3Me{:}CHBr{\cdot}CHBrPh$ is obtained by adding the requisite quantity of bromine to the base dissolved in carbon bisulphide. It crystallises in needles, and melts at 156° with decomposition.

When benzylidene-2 : 6-lutidine is reduced by boiling with sodium and absolute alcohol, a compound of the formula

$$C_5NH_9Me{\cdot}CH_2{\cdot}CH_2Ph$$

is obtained : this can be extracted from the product by ether, and crystallises from alcohol in leaflets. It melts at 80—81°, can be distilled with steam, is insoluble in water, easily soluble in ether, alcohol, benzene, and chloroform; has a strongly alkaline reaction when moistened with water, and has a faint characteristic odour. The *hydrochloride* forms colourless, fern-like crystals, and melts at 141°. The *platinochloride* crystallises in microscopic needles, and melts at 197° with decomposition. The *aurochloride* crystallises in beautiful, long, yellow needles, melts at 166°, and is somewhat easily soluble in alcohol. The *mercurochloride*, $C_{14}NH_{21},HHgCl_3$, is obtained in extremely slender needles, crystallises from alcohol in small leaflets, and melts at 138°.

Dibenzylidene-2 : 6-*lutidine*, $C_5NH_3(CH{:}CHPh)_2$, crystallises in beautiful, long, lustrous needles, melts at 167·5°, has no odour, is without action on litmus, and is insoluble in water, but soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. With hydrochloric acid, it yields an intensely yellow salt, which becomes colourless on drying. The *mercurochloride*, $C_{21}NH_{17},HHgCl_3$, crystallises in yellow needles, melts at 193°, and is insoluble in boiling water, easily soluble in warm alcohol. The *aurochloride* and *platinochloride* crystallise in small needles, and do not melt at 270°. The *picrate* crystallises in slender, yellow needles, turns brown and sinters at 150—160°, and melts at 220°. The *brominated* derivative, $C_5NH_3(CHBr{\cdot}CHBrPh)_2$, crystallises from absolute alcohol in interlacing needles, and melts at 183°.

Tetrahydrodibenzylidene-2 : 6-*lutidine*, $C_{21}H_{21}N$, is obtained by heating dibenzylidenelutidine (3 grams) with fuming hydriodic acid (30 grams) in a sealed tube for two hours at 160°. The product is treated with sulphurous acid, alkali added, and the base extracted

with ether. It crystallises from alcohol in colourless needles, melts at 153°, and is insoluble in water, but easily soluble in alcohol, benzene, ether, and chloroform. The *hydrochloride* crystallises in yellowish needles. The *platinochloride*, $(C_{21}NH_{21})_2,H_2PtCl_6 + H_2O$, crystallises in yellow needles, melts at 79—80°, and is soluble in hot water. The *picrate* crystallises in small needles, and melts at 149°. The *aurochloride* is an oil. E. C. R.

Diethyl Hydrofurfuryllutidinedicarboxylate and its Derivatives. By F. Heiber (*Ber.*, **25**, 2405—2407).—Diethyl hydrofurfuryllutidinedicarboxylate, $N\ll^{CMe\text{———}C(COOEt)}_{CH(C_4H_3O)\cdot CH(COOEt)}\gg CMe$, is obtained by warming a mixture of ethyl acetoacetate (2 mols.) and furfuraldehyde (1 mol.) with a slight excess of concentrated alcoholic ammonia for a few minutes at 40° with constant shaking. It melts at 163·5—164·5°.

Diethyl furfuryllutidinedicarboxylate nitrate, $C_{17}H_{19}NO_5,HNO_3$, is obtained by suspending the ethereal salt in three times the quantity of alcohol and passing nitrous acid into the mixture until a sample dissolves to a clear solution in hydrochloric acid. The product crystallises from dilute alcohol, melts at 118·5—119° with decomposition, and is very sparingly soluble in water, but easily in alcohol or ether. The mother liquors contain small quantities of the free base, which may be converted into nitrate by the careful addition of dilute nitric acid.

Diethyl furfuryllutidinedicarboxylate, $C_{17}H_{19}NO_5$, is obtained by shaking the above nitrate with sodium carbonate. It melts at 40—41°, becomes yellow on exposure to light, is insoluble in water, easily soluble in alcohol and ether, and cannot be obtained crystalline from the latter solvent. The *platinochloride* is obtained as a crystalline precipitate of the composition $(C_{17}H_{19}NO_5)_2,H_2PtCl_6$.

E. C. R.

Sparteïne. By A. Peratoner (*Gazzetta*, **22**, 566—571).—On heating sparteïne (2 grams) with water (30 c.c.) and silver oxide (10 grams) in a closed tube at 170—180° for 4—6 hours, metallic silver and much carbonic anhydride are obtained. On dissolving the product in water, filtering, treating with excess of potash, and distilling from an oil-bath, an aqueous distillate having an odour of pyridine was obtained; at the end of the operation, a few drops of unchanged sparteïne distilled. The aqueous solution thus obtained was neutralised with sulphuric acid and distilled twice, the second time with the addition of hydrochloric acid. The residues in each case were converted into platinochlorides; on concentrating the aqueous solution, sparteïne platinochloride separated. The mother liquors, after concentration and addition of alcohol, yielded two platinochlorides, the more soluble one melting at 238—240°, and the other at 178°. The first consisted of pyridine platinochloride, whilst the second, of which only a very small quantity was obtained, was possibly α-picoline platinochloride. W. J. P.

Quinine Methiodides. By E. Grimaux (*Compt. rend.*, **115**, 117—120).—When quinine dimethiodide is allowed to remain in contact with dilute aqueous potash in the cold for about 24 hours, the principal product is resinous and easily soluble in alcohol, from which it will not crystallise, but there is also formed about 12 per cent. of a yellow, crystalline powder, almost insoluble in neutral solvents. The crystals are slender needles which melt with decomposition at about 280°; they dissolve easily in acids, forming brownish-yellow, gelatinous salts, and the compound is reprecipitated by alkalis. Dilute solutions in alcohol, acetic acid, &c., have an intense, brilliant fluorescence. This compound has, in all probability, a high molecular weight, and is not formed by simple removal of hydriodic acid from the quinine dimethiodide; the proportion of iodine in the compound is lower than that required by the formula $C_{20}H_{24}N_2O_2{\cdot}OH,MeI$.

Methoxyquinoline methiodide, when treated with dilute aqueous potash, yields a crystalline, orange-yellow powder, in all respects similar to that obtained under similar conditions from quinine dimethiodide. It follows that the methyl iodide removable by potash from the quinine derivative is united with the methoxyquinoline group in the quinine molecule, and, since in quinine monomethiodide the methyl iodide is not removable by potash, it follows that the constitution of the monomethiodide is $C_{10}H_7(OMe)NO{\cdot}C_9H_{14}ONMeI$. The nitrogen not belonging to the quinoline nucleus is the more strongly basic, and it would seem that the most probable constitution of the basic salts of quinine is $C_{10}H_7(OMe)NO{\cdot}C_9H_{14}ON,HCl$ and $[C_{10}H_7(OMe)NO{\cdot}C_9H_{14}ON]_2,SO_4H_2$.

When basic quinine sulphate is boiled with excess of methyl iodide in presence of methyl alcohol, it yields quinine dimethiodide, and sulphuric acid is liberated. It would seem that the quinine salt partially dissociates in the boiling methyl alcohol, and the dissociation continues in consequence of the union of the liberated quinine with the methyl iodide. C. H. B.

The Hydriodo-compounds of the Cinchona Alkaloïds. By E. Lippmann and F. Fleissner (*Monatsh.*, **13**, 429—439; compare Abstr., 1891, 1517; this vol., p. 81; Skraup, this vol., pp. 83, 640).—Skraup and his co-workers have recently described a series of dihydriodides of certain cinchona alkaloïds, in which they regard both iodine atoms as combined with carbon atoms; the authors' investigations had led them to believe that the second molecule of hydrogen iodide was combined with the nitrogen atom, and they have therefore repeated Skraup's work, obtaining results which support their former conclusion. The monhydriodides containing the iodine in combination with the carbon behave as bases, the dihydriodides as normal salts, and the trihydriodides as acid salts.

Hydriodocinchonine hydriodide, $C_{19}H_{23}N_2OI,HI$, is formed by making a cinchonine solution neutral or slightly acid with hydriodic acid, and, after crystallisation from water and alcohol, melts at 187—190°; an excess of acid converts it into the trihydriodide already described. The *hydrochloride* and *nitrate* of hydriodocinchonine have also been prepared, and crystallise well.

When quinidine is treated with an excess of hydriodic acid, it is converted into the trihydriodide described by Skraup; this is converted, by the continued action of dilute ammonia, into *hydriodoquinidine*, the reaction not stopping with the formation of the dihydriodo-derivative, as supposed by Skraup; there is, therefore, no reason to suppose that in this compound the second iodine atom is also combined with the carbon. The following salts of hydriodocinchonine have also been prepared: the *platinochloride*, $C_{20}H_{25}N_2O_2I,H_2PtCl_6$, crystallising in orange-yellow plates; the *acid sulphate*,

$$C_{20}H_{25}N_2O_2I,H_2SO_4,3H_2O,$$

in silky needles; the *normal nitrate*, $C_{20}H_{25}N_2O_2I,HNO_3$, in feathery needles; the *acid nitrate*, $C_{20}H_{25}N_2O_2I,2HNO_3$, in strongly-refractive prisms; and the *acid hydrochloride*, $C_{20}H_{25}N_2O_2I,2HCl$, in feathery groups of silky needles. The *hydriodide*, $C_{20}H_{25}N_2O_2I,HI$, is obtained by the action of the theoretical quantity of ammonia on the trihydriodide, and has the physical properties ascribed to it by Skraup.

Skraup and Schubert, in their investigation of the action of ammonia on quinine trihydriodide, came to the conclusion that the product was a mixture of two distinct bases, of the composition $C_{20}H_{25}N_2O_2I$ and $C_{20}H_{26}N_2O_2I_2$, respectively, and that the original product was a mixture of two isomeric salts, $C_{20}H_{25}N_2O_2I,HI$ and $C_{20}H_{26}N_2O_2I_2,2HI$. The latter conclusion the authors find to be incorrect, the substance examined being, in reality, incompletely decomposed. If the mixture of the trihydriodide and aqueous ammonia is shaken with ether and allowed to remain, asymmetric crystals separate, containing ether of crystallisation and having the composition $C_{20}H_{25}N_2O_2I + Et_2O$; if kept over sulphuric acid in a vacuum, they lose $\frac{1}{2}$ mol. ether, the latter being completely removed in a current of hydrogen at 60°. Hydriodoquinine is thus obtained as a voluminous, dull, white powder, which melts at 150—155°, but commences to decompose at a much lower temperature.

H. G. C.

Condensation of Aldehydes with Benzoylpiperidine. By L. Rügheimer (*Ber.*, **25**, 2421—2429; see also Abstr., 1891, 1246).—The author finds that the compound obtained by treating benzoylpiperidine with benzaldehyde has the composition $C_{19}H_{17}N$, and not $C_{19}H_{19}N$, and is dibenzylpyridine.

Dibenzylpyridine, $C_5NH_3(CH_2Ph)_2$, is obtained by heating benzaldehyde (6 parts) with benzoylpiperidine (5 parts) in a sealed tube at 240—250° for six hours. The product is dissolved in ether, the ethereal solution shaken with sodium hydroxide and then with dilute hydrochloric acid. The base is obtained in the aqueous layer as hydrochloride, which sinks as a heavy oil crystallising after a time, and is purified by boiling it with a small quantity of benzene and allowing it to crystallise. The *free base* is obtained by dissolving the hydrochloride in chloroform and shaking the solution with sodium hydroxide; it crystallises from alcohol in thin tablets and scales, melts at 89°, and is easily soluble in alcohol, ether, and chloroform. It is a feeble base, and the salts are decomposed by water. The *hydrochloride* crystallises from benzene in large plates and scales, falls

to a powder on exposure to air, melts under boiling benzene, and, when dry, melts at 164·5—166°. The *hydrobromide* crystallises from benzene in thin plates, melts at 148·5° (uncorr.), and falls to powder on exposure to air. The *methiodide* is an oil which will not crystallise, and when its solution in chloroform is evaporated, yields leaflets which contain chloroform, and become oily on exposure to air. The *ethiodide* crystallises from alcohol in small needles, melts at 137°, is sparingly soluble in water, very sparingly so in benzene, but easily in chloroform.

Dibenzoylpyridine, $C_5NH_3Bz_2$, is obtained by heating the above base (1 part) with potassium dichromate (4·5 parts) and sulphuric acid (7 parts) in a reflux apparatus for 6—8 hours. The product is dissolved in acetic acid, the filtered solution diluted, treated with excess of sodium hydroxide, and the precipitate thus formed is dried at the ordinary temperature and extracted with boiling ether. It crystallises from alcohol in long needles, melts at 123°, is somewhat soluble in hot water, and is a feeble base. The *platinochloride* is obtained in long, bright, reddish-yellow needles, and cannot be recrystallised without decomposition.

When dibenzylpyridine (8 grams) is treated with chromic anhydride (75 grams) and sulphuric acid (260 grams diluted with twice its volume of water), it yields benzoic acid, benzoylpyridinecarboxylic acid, and pyridinedicarboxylic acid. The dicarboxylic acid does not melt at 290°, and the author believes it to be the 3.5-acid.

Tribenzylpyridine, $C_5NH_2(C_7H_7)_3$, is obtained in a similar way to the dibenzyl compound, by employing a larger proportion of benzaldehyde. It is insoluble in ether, crystallises from amyl alcohol, in which it is sparingly soluble, in small leaflets and plates, melts at 278—280°, and is very sparingly soluble in alcohol, easily so in acetic acid. E. C. R.

2 : 3-Dipiperidyl. By F. Blau (*Monatsh.*, **13**, 330—343).—The author has corrected and extended his previously published work on this compound (compare Abstr., 1891, 583). The base, when purified by distillation with steam, is a powerful alkali, boils at 267—268°, and melts at 68—69°. The true melting point is, in all probability, somewhat higher than this, for the compound rapidly absorbs water and carbonic anhydride from the air, and the temperature of fusion is thereby lowered. The *platinochloride*, $C_{10}H_{20}N_2,H_2PtCl_6 + 2H_2O$, is readily soluble in water, melts at 237—238° and loses its water of crystallisation at 100°; the *aurochloride*, $C_{10}H_{20}N_2,2HAuCl_4$, melts at 211—212°, and the *picrate* at 215°. *Nitrosodipiperidyl*, $C_{10}H_{19}N_2(NO)_2$, has the characteristic odour of the nitrosamines, is not readily soluble in water unless a free acid is present, melts at 87·5—88·5°, and on long-continued warming with concentrated hydrochloric acid is partly reconverted into the original base. The compound of 2 : 3-dipiperidyl with carbon bisulphide crystallises well, and melts at 205° with decomposition.

The author has also carried out the reduction of nicotine according to Liebrecht's method (Abstr., 1886, 161), but has obtained a mixed product in lieu of that investigator's so-called dipiperidyl (hexahydro-

nicotine), which boils at 250—252°. It boils at 235—265°, and has not yet been completely investigated. G. T. M.

Hyoscine. By A. Ladenburg (*Ber.*, **25**, 2388—2394).—An answer to a paper by Schmidt (this vol., p. 1255). Schmidt has stated his belief that hyoscine, $C_{17}H_{23}NO_3$, does not exist, but is identical with scopolamine, $C_{17}H_{21}NO_4$, and says that the author's analyses agree better with the latter than with the former formula. The author quotes analyses which show that this is not the case. The basic decomposition product of hyoscine, that is, pseudotropine, also gave on analysis of its salts numbers agreeing with the author's formula.

The author has again analysed hyoscine aurochloride,

$$C_{17}H_{23}NO_3,HAuCl_4,$$

and pseudotropine platinochloride $(C_8H_{15}NO)_2,H_2PtCl_6$, and confirms his former results.

Pseudotropine platinochloride crystallises in the rhombic system; $a : b : c = 0{\cdot}70586 : 1 : 1{\cdot}39935$. These crystals are crystallographically distinct from those of scopoline platinochloride.

The author has examined a commercial sample of hyoscine, and finds that it contains scopolamine. This is, however, of no consequence commercially, as the two compounds have the same therapeutic action.

The author suggests the name *isidiom* for compounds which have different compositions but are very similar in chemical behaviour: such compounds are hyoscine and scopolamine, pseudotropine and scopoline, cobalt and nickel, niobium and tantalum pentachlorides, benzene and thiophen, &c. E. C. R.

Alkaloïds of the Root of Corydalis cava. By M. Freund and W. Josephy (*Ber.*, **25**, 2411—2415).—The product which the authors employed was obtained from Trommsdorff's manufactory, in Erfurt, and is prepared as follows:—The finely-cut roots are extracted with alcohol, the alcohol distilled off, and the aqueous solution which remains filtered from resin; ammonia is then added to the filtrate, and the precipitated base extracted with ether. On concentrating the ethereal solution, a product is first obtained which melts about 160°, but the mother liquors, if further concentrated and mixed with alcohol, yield a crystalline precipitate, which is purified by recrystallisation from alcohol. The product thus obtained melts at 126—130°, and is known as "corydaline"; the authors have examined it, however, and find that it consists of at least three alkaloids.

Corydaline, $C_{22}H_{27}NO_4$, melts at 134·5°. The authors confirm the results of Dobbie and Lauder (Trans., 1892, **61**, 244, 605).

Bulbocapnine, $C_{34}H_{36}N_2O_7$, is separated from corydaline by using excess of alkali, in which it is soluble, whereas corydaline is not. It melts at 198—199°, does not lose water when heated at 120°, and is bibasic.

Corycavine, $C_{23}H_{23}NO_5$, is contained in small quantity in the crude product melting at 126—130°, and in somewhat larger quantity in the product melting at 160°. It melts at 214—215°, crystallises in beautiful, rhombic tablets, is insoluble in alkali and less soluble in absolute alcohol than corydaline. The *hydrochloride*,

$$C_{23}H_{23}NO_5,HCl,H_2O,$$

the *hydriodide*, $C_{23}H_{23}NO_5,HI,H_2O$, and the *platinochloride*,

$$(C_{23}H_{23}NO_5)_2H_2PtCl_6,2H_2O,$$

do not lose their water of crystallisation when heated at 120—130°. The *methiodide* melts at 218°.

The authors have also examined preparations of corydaline obtained from E. Merck, of Darmstadt, and from T. Schuchardt, of Görlitz. The former contained corydaline and bulbocapnine. The latter contained corydaline and a small quantity of a base which is soluble in alkali, and melts at 205—207°.

The authors are engaged in the further study of bulbocapnine and corycavine. E. C. R.

A New Leucomaïne. By A. B. Griffiths (*Compt. rend.*, **115**, 185—186).—A considerable quantity of the urine of an epileptic was made alkaline with sodium carbonate, shaken with half its volume of ether, the filtered ethereal extract agitated with aqueous tartaric acid, and the alkaloïd precipitated from the acid solution by excess of sodium carbonate. It was then taken up with a fresh quantity of ether, and on evaporating the latter, was left as white, oblique prisms. The *leucomaïne*, $C_{12}H_{16}N_5O_7$, thus obtained, is soluble in water, is feebly alkaline in reaction, and forms a crystalline *hydrochloride* and *aurochloride*. It gives a greenish-white precipitate with mercuric chloride, a yellowish precipitate with silver nitrate, a white precipitate with phosphotungstic acid, a brownish-white precipitate with phosphomolybdic acid, and a yellow precipitate with tannin. It is poisonous, producing trembling, intestinal and urinary evacuations, dilatation of the pupils, convulsions, and death. Jn. W.

Physiological Chemistry.

Digestibility of Raw and Boiled Meat. By A. Stutzer (*Landw. Versuchs-Stat.*, **40**, 321—322).—Nearly all the results of experiments on the digestibility of meat show that it is made less digestible by being cooked. The author has investigated the matter, using his own method of fractional digestion. A large piece of beef was cut in half, the one half cut up, dried at 40°, and finely powdered. The other half was boiled in the usual manner, but without salt, cut up, dried at 40°, and powdered. The following analytical results were obtained :—

	Nitrogen per cent.			Moisture per cent.
	Non-proteïd.	Soluble in pepsin.	Insoluble in gastric juice.	
Raw meat.....	1·33	12·73	0·35	5·25
Boiled meat	0·49	13·07	0·43	6·92

The meat (about 4 grams) was then treated with dilute hydrochloric acid (0·05 and 0·2 per cent.) and with gastric juice containing 0·05 and 0·20 per cent. of hydrochloric acid; the percentage amounts of nitrogen digested were as follows:—

	Nitrogen dissolved.	
	Raw meat.	Boiled meat.
Gastric juice (0·05 per cent. HCl)	89·2	38·7
,, ,, (0·20 ,, ,,)	96·9	79·3
Hydrochloric acid (0·05 per cent.)	29·0	9·6
,, ,, (0·20 ,,)	52·2	13·2

Boiling thus diminishes the digestibility of meat, the difference being most considerable when a small amount of hydrochloric acid is used. N. H. M.

Presence of Pentamethylenediamine in Pancreas Extracts. By B. Werigo (*Chem. Centr.*, 1892, i, 487—488; from *Pfluger's Arch.*, **51**, 362—366).—The finely-divided pancreas is digested for 24 hours with five times its weight of water, together with a little chloroform, heated to boiling, and filtered. On adding picric acid to the filtrate, a precipitate is formed, which is principally amorphous, but also includes some crystalline substance. As obtained by the author, this substance appeared to be isomeric with Brieger's cadaverine. Whether it is formed by fermentation or not is doubtful.

In one specimen which had been prepared six months previously and was still sterile, a little of this substance could be detected; the author thinks it probable that it is formed by the action of an enzyme. J. W. L.

Human Succus Entericus. By A. H. Tubby and T. D. Manning (*Guy's Hosp. Rep.*, **48**, 271—298).—A case is recorded in which by surgical interference a Vella's fistula was made. The pure intestinal juice was collected by means of a sponge, or an appropriate bottle strapped to the patient's side. The daily average quantity was about 25 c.c. Its reaction was alkaline; its average sp. gr. 1·0069. By artificial digestion experiments, it was found to cause a flocculent precipitate (caseïnogen?) in milk, the milk turning acid; it also prevented the gelatinisation of gelatin. It had no proteolytic action on proteïds. It emulsified and saponified fats. But the most important property of the juice appeared to be its action on carbohydrates. This is in accordance with the most trustworthy previous work on

the subject. Cellulose was unaltered; starch was in 56·5 per cent. of the experiments converted into dextrose; and in 60 per cent. of the experiment, sucroses (cane sugar and maltose) were converted into glucose. Succus entericus thus continues the action of the salivary and pancreatic ferments. A glycerine extract of the mucous membrane was made which acted in the same way. W. D. H.

Influence of Oxygen on the Separation of Carbonic Anhydride in the Lungs. By B. Werigo (*Chem. Centr.*, 1892, i, 488; from *Pfluger's Arch.*, **51**, 321—361).—In order to determine whether or not oxygen displaces carbonic anhydride from the blood in the lungs merely by the laws of gaseous diffusion, the author caused each lung of the same animal to work independently of the other. To the one lung, a gaseous mixture rich in oxygen; to the other, an inert gas (hydrogen) was supplied. The results corroborate those obtained by Pflüger, and afford further evidence that the carbonic anhydride is displaced by oxygen in accordance with the ordinary laws of gaseous diffusion. J. W. L.

Combination of Hæmoglobin with Oxygen. By C. Bohr (*Chem. Centr.*, 1892, i, 486—487; from *Skand. Arch. Physiol.*, 1891, iii, 76).—The author distinguishes between different oxyhæmoglobins (Abstr., 1890, 1450) which absorb different quantities of oxygen.

The α-modification may be obtained in solution if the solution of the β-modification is placed in a vacuum, and then shaken with air. From the usual crystalline γ-modification the β-modification may be obtained by repeatedly drying and redissolving the crystals. The γ-modification may be obtained directly from blood by separating the blood corpuscles by means of a centrifugal machine, and then washing with sodium chloride solution to which a little ether has been added. The δ-modification was frequently formed in some specimens of the γ-modification which had been preserved in solution in sealed tubes.

There appears to be no uniform relation between the quantities of absorbed oxygen, the dry substance, the proportion of iron, and the absorption of light of the several modifications. The proportion of iron varied from 0·32 to 0·47 per cent., and the relative molecular weight varied very greatly. J. W. L.

Sensitiveness of the Hæmatin Spectrum and the Formation of Hæmin Crystals as Proof of the Presence of Blood. By G. Janeček (*Chem. Centr.*, 1892, i, 507—508).—Of the three methods which are generally employed for the detection of blood, the microscopical examination of the corpuscles, the examination of the hæmatin spectrum, and the preparation of hæmin crystals, the former is undoubtedly the best, provided that the material at command will admit of such an examination. The author has, however, made some very interesting observations regarding the blood and excrement of insects, such as fleas and bugs, which live on higher animals. He finds that not only the blood, but also the excrement contains the perfect blood corpuscles of the higher animals from which it was originally obtained. Consequently the

spectrum of these materials was very similar to that of the blood of the higher animal, and the hæmin crystals could be obtained in quantity. J. W. L.

Hæmocyanin. By L. Fredericq (*Compt. rend.*, **115**, 61).—The author confirms the statements of Krukenberg, Halliburton, Griffiths, and others. He considers that the negative results obtained by Heim (this vol., p. 898) are due to the fact that Heim made his experiments with the cray fish, lobster, crab, &c., in which the quantity of hæmocyanin is very small. C. H. B.

Respiratory Value of Hæmocyanin. By L. Cuénot (*Compt. rend.*, **115**, 127—129).—The author has compared the quantity of oxygen present in the blood of *Helix pomata* with the quantity dissolved in the distilled water of the laboratory. The results show that the blood contained from 11 to 12 c.c. of oxygen per litre, a quantity considerably greater than is dissolved by water in contact with air.

It follows that hæmocyanin has a distinct power of absorbing oxygen, although in this respect it is much inferior to hæmoglobin. It would seem, therefore, to have a true respiratory function, but this is so feeble that the replacement of the hæmocyanin by a colourless proteïd which has no chemical attraction for oxygen does not materially affect the vital processes of the organism. As a matter of fact, under similar conditions, allied species occur, some with and some without hæmocyanin. The presence of hæmoglobin in invertebrata, on the other hand, is generally observed where the conditions of life are difficult, especially as regards the supply of oxygen required for respiration (compare this vol., p. 898 and preceding abstract). C. H. B.

Cause of the Rapid Curdling of Milk during Thunder Storms. By Liebig (*Chem. Centr.*, 1892, i, 490—491; from *Milch. Zeit.*, 1891, No. 27).—Experiments made with a view of demonstrating whether the increased proportion of ozone present in the atmosphere at the time of thunder storms is the cause of the rapid curdling of milk gave negative results; and the author considers that it is the high temperature which usually accompanies such atmospheric conditions which indirectly causes the souring; such temperatures being favourable to rapid fermentation. J. W. L.

Chemistry of Vegetable Physiology and Agriculture.

Calcium Oxalate in the Bark of Trees. By G. Kraus (*Ann. Agron.*, **18**, 271—272).—As the result of his experiments on the barks of various trees which contain calcium oxalate in quantity, the author concludes that this is a reserve deposit and not an excretion, and that it is redissolved in spring and summer according to the

needs of the plant. Branches of *Ribes sanguineum* lost, from December 16th to April 27th, 16·62 per cent. of their oxalate; from March 13th to April 3rd, 13·17 per cent.; and to April 16th, 38·07 per cent. Similar results were obtained with other trees. The author remarks that calcium oxalate is certainly liable to solution by long-continued action of an acid circulating liquid like cell-sap.

J. M. H. M.

Occurrence in Plants of a Gum giving rise to Xylose by Saccharification. By A. Hébert (*Ann. Agron.*, **18**, 261—267).—The author points out that the probability of the formation of carbohydrates in plants by the polymerisation of formaldehyde is strengthened by the recent discoveries of carbohydrates having other than 6 atoms of carbon: the pentaglucoses, such as arabinose and the xylose of Wheeler and Tollens; and the heptaglucose formed by Muntz and Marcano by hydrolysis of the perseïtol ($C_7H_{16}O_7$) extracted from *Laurus persea*.

The wood-gum yielding xylose by saccharification, originally found in several species of wood by Wheeler and Tollens, has since been found in large quantity by the author in oat straw and wheat straw; he now shows that the hay of grasses contains it in quantity, and that lucerne contains little or no starch, but is rich in the same straw- or wood-gum. Flax straw also contains much of it.

The melting point and rotatory power of the sugar produced by hydrolysis of the gum extracted from these products agree with those of xylose, as do the melting point and character of the crystalline osazone which it yields by treatment with phenylhydrazine. By a less direct test (namely, the production of furfuraldehyde, a characteristic product of the pentaglucoses when acted on by boiling mineral acids) the author infers the presence of the same gum in many other vegetable products, including beet and potato pulp residues and the leaf mould of gardeners.

J. M. H. M.

Preparation of Teas. By Y. Kozai (*Bied. Centr.*, 1892, 488—489).—Young leaves gathered from tea shrubs of different ages, but growing on the same plot of ground, show no definite variation in their composition which can be attributed to the age of the plant. If the shrub, for three weeks before picking, be encased so as to exclude the light, the leaves are etiolated, and vary in composition from those grown in full light.

	Grown in the dark.	Grown in the light.
Theïne	4·532 p. c.	3·784 p. c.
Total nitrogen	7·835 „	6·945 „
Nitrogen in theïne	1·311 „	1·094 „
Percentage of theïne nitrogen on total nitrogen...	16·72 „	15·75 „

The percentage of tannin is not affected by excluding the light. In Japan, the finest tea, after powdering, is consumed with the liquor: by another method the leaves are steeped for two minutes in water at 50—60°; a poorer quality is obtained by treatment for one minute

in boiling water: by the use of water at 50° three extractions may be made, each differing very slightly from one another in composition; whilst if the water is at 100°, then nearly all the soluble matter is removed by the first steeping. E. W. P.

Influence of Phosphoric Acid on the Formation of Chlorophyll. By O. Loew (*Ann. Agron.*, **18**, 270—271).—Hoppe-Seyler, in 1879, found that "crystallised chlorophyll" contained 1·38 per cent. of P_2O_5; and later, that chlorophyll, when treated with boiling alcoholic potash is resolved into choline, glycerophosphoric acid, and the acid of chlorophyllane, and suggested that chlorophyll is probably a kind of lecithin in which the acid of chlorophyllane plays the part of a fatty acid. Struck with this view, and following up an observation of his own, the author cultivated *Spirogyra majuscula* in a nutrient solution containing, per thousand, 0·2 of calcium nitrate and 0·02 of ammonium sulphate. The cultures were made in stoppered flasks, into which a little carbonic anhydride was introduced from time to time. Elongation of the cells took place, but the increase in mass was insignificant, cell division not being noticed. Many cells had become swollen, and had given out lateral tubes, as if in preparation for conjugation. The chlorophyll layer was pale and yellowish, but continued its movements, although sluggishly. On adding 0·02 per 1000 of ferrous sulphate and dividing the cultures into two lots, to one of which was added 0·08 per 1000 of disodium phosphate, a great difference was observed. After five days, those cultures which received phosphoric acid became dark green, cell division took place, and the chlorophyll movement became lively. The cultures receiving iron alone did not show this recovery. J. M. H. M.

Analyses of Apple Tree Leaves. By F. T. Schutt (*Bied. Centr.*, 1892, 493—494).—The following is the average composition of leaves from five varieties of apple trees, collected on May 25th and September 20th:—

	May 25th.	Sept. 20th.
Water	73·36 per cent.	60·71 per cent.
Ash	2·33 ,,	3·46 ,,
Nitrogen	2·94 ,,	2·48 ,,
	In Ash.	
P_2O_5	10·47 ,,	5·82 ,,
K_2O	10·82 ,,	11·63 ,,
CaO	17·40 ,,	27·91 ,,
MgO	9·77 ,,	4·81 ,,
Fe_2O_3	1·49 ,,	1·41 ,,
SiO_2	1·07 ,,	1·14 ,,

E. W. P.

Analyses of Healthy and Diseased Sugar Cane. By A. Stutzer (*Landw. Versuchs-Stat.*, **40**, 325—327).—The sugar canes were sent from Cheribon, in Java, in 1884, when there was much disease. The healthy plant was 2—2·5 m. high, and the average

circumference of the stalk 9—11·5 cm.; the pith was white. The diseased cane (of the same age as the other) had stalks 50—60 cm. high, and many less. Many plants had no stalks, the leaves growing from the root stem; the leaves were smaller than those of the healthy plant, and the pith was more or less brown, and was frequently wanting altogether. The following table shows the percentage of ash constituents in the dry substance of (I) healthy leaves, (II) diseased leaves, (III) healthy canes, (IV) diseased canes:—

	SiO_2.	SO_3.	P_2O_5.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Cl.
I...	3·032	0·466	0·307	0·053	0·080	0·310	2·022	1·504	0·552
II...	9·348	0·384	0·467	0·509	0·310	0·360	1·213	1·945	0·694
III...	0·950	0·154	0·269	0·067	0·040	0·063	0·990	0·690	0·150
IV...	1·504	0·305	0·410	0·048	0·035	0·056	1·640	0·516	0·309

The percentages of nitrogen were—(I) 0·65, (II) 0·76, (III) 0·35, (IV) 0·64.

The differences in the ash constituents are considerable, especially in the case of potash and silica, and when the analyses of the healthy cane are compared with earlier analyses (Knop, Abstr., 1883, 110; 1884, 1212), it is seen that the amounts of lime and magnesia are low, whilst that of soda is very high. The results with the analyses of the soil in which the plants were grown indicate that a manuring with potash and lime is most necessary, especially as sugar cane is known to thrive well in a calcareous soil. Almost the only manure employed is "böngkil," consisting of earth-nut cake containing a good deal of oil, about 5 per cent. of nitrogen, and scarcely 1 per cent. of phosphoric acid and potash respectively. N. H. M.

Some Properties of Humin and Humic Acid. By Miss A. Rodzyanko (*J. Russ. Chem. Soc.*, **22**, 208—229).—Experiments of the authoress on earth obtained from the Government of Poltawa have shown that, when minerals are acted on by humic acid, acid salts are formed, and also other compounds, containing the elements of the minerals united with the radicle of this acid. Humin absorbs various inorganic substances from aqueous solution, such as the salts of sulphuric, hydrochloric, phosphoric, and carbonic acids, solutions of aluminium chloride and of alkaline silicates. Humic acid dissolves and decomposes several otherwise insoluble inorganic compounds; it decomposes the silicates. Compounds which belong to the class of alcoholic derivatives are formed.

Humin compounds already containing a given element absorb substances containing this element more readily than other substances; it seems that metallic derivatives of humic acid are stronger acids than the original acid, and the constitution of the metallic derivatives of organic compounds present in a given sample of earth naturally depends on its original composition. M. F.

Analytical Chemistry.

Improved Gas Pipette. By A. H. Gill (*Zeit. anal. Chem.*, **31**, 292—293).—In place of the four-bulb Hempel pipette, the author uses that with two bulbs only, but attaches an india-rubber ball to the wider tube. This protects the reagents as effectually as the water lute, and is more convenient in use. M. J. S.

Errors arising in Chemical Operations owing to the Employment of Gas Flames. By A. Lieben (*Monatsh.*, **13**, 286—298).—Coal-gas contains an appreciable amount of combined sulphur; and, when its flame is directly employed in the evaporation of solutions contained in open dishes, sulphur, in the form of sulphuric acid, can be usually recognised in the solutions. The quantity of sulphur absorbed as sulphuric acid by any particular liquid, during evaporation, depends not only on the size of the flame and on the duration of the process, but also on the chemical properties of the liquid in question. The largest quantity of acid is absorbed by solutions of substances having a basic nature, and by those containing the salts of volatile organic acids. Much less sulphur is absorbed during the evaporation of distilled water, and very little indeed by a solution of barium chloride acidified with hydrochloric acid. Pure hydrochloric acid does not take up even a trace of sulphuric acid.

Under some conditions, sulphurous anhydride can be recognised amongst the products of combustion of coal gas; but even then it is produced only in very small quantities. The formation of sulphuric acid must not therefore be regarded as due to the oxidation of the lower oxide. This view is confirmed by the fact that when a platinum dish filled with water is placed over a Bunsen flame, the dewy deposit, which immediately forms on the outside, contains a considerable quantity of sulphuric acid. On further heating, this water volatilises; but the sulphuric acid, owing to its high boiling point, remains on the platinum. G. T. M.

Extended Employment of Arsenious Acid in Volumetric Analysis. By R. Namias (*Gazzetta*, **22**, 508—513).—The author dissolves arsenious oxide (8 grams) in a concentrated aqueous solution (300—400 c.c.) of ammonium acetate (80 grams) by the aid of heat, and then dilutes to a known volume (1 litre). This solution is standardised against iodine solution of known strength (10 grams of iodine per litre) and need not be titrated in presence of sodium hydrogen carbonate, as equally accurate results are obtained when the solution contains free acetic acid. The titration with the acid solution is less rapid than with the ordinary alkaline solution, but can be performed more quickly at 60—70° with no diminution in accuracy.

The estimation of the active chlorine in bleaching powder may be conducted as follows:—The bleaching powder (10 grams) is triturated in a mortar with water and the liquid made up to a litre. 15 c.c. of the

standard arsenious oxide solution is added to 10 c.c. of the clear bleaching powder solution, heated to 60°, acidified with acetic acid, and the excess of arsenious solution titrated with iodine solution in presence of starch. Chloric acid may be estimated by adding the chlorate (0·5 gram) to the arsenious solution (20 c.c.), diluting to 50 c.c., adding excess of hydrochloric acid, heating at 100° for some time, and titrating with iodine. The determination of the active oxygen in manganese dioxide may be made in a similar manner.

Chromates and dichromates may be estimated in the same manner as manganese dioxide or in a solution acidified with acetic acid only; in this case the liquid must be boiled for at least 15 minutes before the titration is performed.

The volumetric estimation of lead may be carried out as follows:—An excess of potassium dichromate solution of known strength is added to the solution of the lead salt acidified with acetic acid. The liquid is now made up to a known bulk, and after complete subsidence of the precipitate an aliquot part of the solution is withdrawn and the excess of dichromate found by means of the arsenious solution. The results are accurate, but if the titration is performed in presence of the precipitate the results are somewhat less trustworthy.

W. J. P.

Presence of Lead in Glass Wool. By L. Blum (*Zeit. anal. Chem.*, **31**, 292).—A specimen of commercial glass wool was found to blacken when exposed to hydrogen sulphide, the blackening being due to the presence of lead. For the filtration of acids, or any operation in which the presence of lead would be objectionable, such wool must be avoided.

M. J. S.

Gasometric Estimation of Nitric Acid. By Glaser (*Zeit. anal. Chem.*, **31**, 285—288).—In those methods which depend on the reduction of the nitric acid by hydrochloric acid and ferrous chloride, and measurement of the nitric oxide, there is always a liability to error from the presence of dissolved oxygen in the liquid over which the gas is collected, whereby part of the nitric oxide is converted into nitrous acid. This oxidation can be prevented by collecting the gas over a 1 per cent. solution of potassium iodide, when the well-known reaction between nitrous and hydriodic acids, resulting in the liberation of iodine and nitric oxide, occurs. In cases where carbonates are present the gas must be treated with soda, but in their absence this is unnecessary. The few test analyses communicated are perfectly satisfactory.

M. J. S.

Estimation of Sulphur.—II. By F. P. Treadwell (*Ber.*, **25**, 2377—2382).—In a former paper (Abstr., 1891, 1137), the author has shown that sulphur can be determined in insoluble sulphides by heating them with iron in an atmosphere of carbonic anhydride, decomposing the sulphide of iron with hydrochloric acid, and absorbing the hydrogen sulphide in an ammoniacal solution of hydrogen peroxide. This method is applicable to the estimation of pyrites in slate if the compound contains no calcium sulphate. If sulphates are present they are reduced to sulphides.

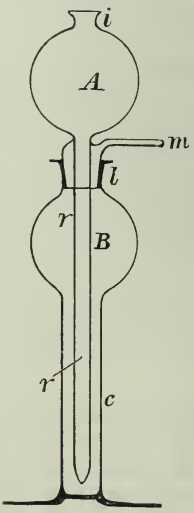
The author finds that the sulphur of pyrites and of other insoluble

sulphides is quantitatively converted into hydrogen sulphide by treatment with tin and concentrated hydrochloric acid.

The analysis is carried out as follows:—The flask in which the decomposition takes place is covered on the bottom with a layer of tin powder 5 mm. thick, and the substance to be analysed, wrapped in tinfoil, is introduced and covered with 60 mm. of granulated tin. The air in the apparatus is then replaced by hydrogen, concentrated hydrochloric acid added, and the mixture heated for about 50 minutes; the hydrogen sulphide which is evolved being collected in hydrogen peroxide solution as previously described. The results obtained are good. The method is applicable to the estimation of pyrites in slate, but slightly high results are obtained.

With substances containing arsenic and antimony, large quantities of arseniuretted and antimoniuretted hydrogen are evolved. The author is engaged on experiments to determine if the reaction is quantitative. E. C. R.

Absorption Apparatus for Use in the Estimation of Sulphur in Iron. By L. Blum (*Zeit. anal. Chem.*, **31**, 290—292).—This consists of two parts, B, a cylinder, the upper part of which is expanded into a bulb of 200 c.c.; A, a tube *r*, drawn out to a point below, and with a 200 c.c. bulb blown on its upper portion, and carrying below its bulb a hollow stopper ground into the neck *l* of the cylinder, and furnished with a side tube *m*, for the escape of unabsorbed



gases. The cylindrical part of B is 20 cm. high, and holds about 50 c.c. In the cylinder is placed either a solution of bromine in hydrochloric acid, or ammoniacal hydrogen peroxide, and the neck *i* of the bulbed tube A is connected by a tube to the flask in which the iron is being dissolved. The whole is stood in a beaker of cold water

while the absorption is taking place. The absorption of the hydrogen sulphide is always complete, and regurgitation of the liquid is impossible.

When brominated hydrochloric acid is used as the oxidising agent, the difficulty in the filtration caused by the presence of resinous brominated hydrocarbons (Abstr., 1890, 921) may be got rid of by adding to the liquid a fragment of ash-free filter-paper before precipitating with barium chloride. This, during the subsequent boiling, breaks up into fibres, which entangle the brominated compounds, promote rapid subsidence of the precipitate, and allow filtration to proceed unchecked. M. J. S.

Volumetric Estimation of Sulphuric Acid in Urine. By E. Freund (*Chem. Centr.*, 1892, i, 607; from *Wien. klin. Woch.*, **51**, 958).—To 50 c.c. of urine (which must not be too strongly coloured) is added 10 drops of a 1 per cent. solution of sodium alizarinsulphonate, and then a 5 per cent. solution of acetic acid is added drop by drop, until the solution becomes orange-coloured; 5 c.c. more of acetic acid are now added, the solution heated nearly to boiling, and titrated with barium acetate until the precipitated barium sulphate appears distinctly red. The barium acetate solution contains 11·22 grams per litre. The experimental error amounts to about 2·5 per cent.

Very concentrated urines are diluted before titration. Strongly coloured urines should be decolorised by the addition of zinc-dust, and the dissolved zinc precipitated by means of sodium hydroxide. J. W. L.

Volumetric Estimation of Sulphates. By A. Bouriez (*Chem. Centr.*, 1892, i, 570—571; from *Rev. internat. fals. aliment.*, **5**, 118—120).—A standard solution of barium hydrogen phosphate is prepared, and with a measured quantity of this the solution of the sulphate is boiled; the barium must be in excess. After filtering from the precipitated barium sulphate, an excess of sodium carbonate is added to the filtrate, which precipitates the excess of barium as tribarium phosphate. This precipitate is washed until the washings are neutral to phenolphthaleïn. The precipitate is transferred to a beaker, dissolved in dilute hydrochloric acid, an excess of sodium sulphate is added to precipitate the barium, and the phosphoric acid is determined in the filtrate volumetrically by Jolv's method, which depends on the fact that methyl-orange reacts with phosphoric acid as a monobasic, whilst phenolphthaleïn reacts with it as a bibasic acid. The solution (which need not be filtered) is therefore coloured with methyl-orange, and standard sodium hydroxide added until the colour becomes orange, inclining to yellow; phenolphthaleïn is then added, and the titration continued until the rose colour appears. From the amount of phosphoric acid found, the amount of sulphuric acid may be calculated. J. W. L.

Estimation of Calcium Salts in Syrup and Sugar Products. By J. Wolf (*Chem. Centr.*, 1892, i, 650; from *Österr.-ungar. Zeit. Zuck.-ind.*, **21**, 96—104).—For this purpose a soap solution is prepared as follows:—150 grams of pure olive oil is warmed on

the water-bath with 5 c.c. of water; 100 grams of finely powdered litharge and a solution of 5 grams of lead acetate in 40 c.c. of water are added, and the whole is stirred until homogeneous. This lead plaster is washed with water and rubbed down (150 grams) with potassium carbonate (40 grams) to a uniform paste, which is extracted with strong alcohol. The lead carbonate is filtered off and the filtrate distilled; 40 grams of the residual soap is then dissolved in 1000 c.c. of alcohol of 56 Tralles. To bring this solution to such a strength that 1 c.c. shall correspond to 0·0005 gram of CaO, 100 c.c. of a solution of calcium chloride (0·15 gram per litre) is introduced into an Erlenmeyer flask, and 25 c.c. of a pure sugar solution of 13° S. (?) added, together with a few drops of strong ammonia; it is then made up to 150 c.c. with water. To this mixture the soap solution is added until a final drop produces a lather about 1 cm. thick, and permanent for 10 minutes. The operation is repeated with the same quantity of the same sugar solution, omitting the calcium chloride solution. The difference between the number of c.c. used in each case is the quantity of soap solution equivalent to 100 c.c. of the calcium chloride solution.

The above solution will serve for titrating the calcium salts in sugar products, provided:—(1) That the liquid is neutral or slightly alkaline. (2) That a few drops of strong ammonia are present. (3) That the quantity of soap solution added does not exceed 20 c.c.; otherwise lime soap separating on the surface will render the end reaction indistinct. (4) When titrating second or third products, the syrups are dissolved in water at about 40°. (5) That the lather is about 1 cm. thick, is clear, vesicular, and permanent for 10 minutes; when the lather has disappeared, it should be easily reproduced by re-agitation.

A. G. B.

Separation and Estimation of Lead, Silver, and Zinc in Galena and Blende. By E. Aubin (*Bull. Soc. Chim.* [3], **7**, 134—135).—The author recommends the following rapid process for the commercial analysis of galenas and blendes. The powdered mineral (10 grams) is treated with fuming nitric acid (50 c.c.) in a conical flask (1 litre); the whole is then evaporated to dryness on the sand-bath, taken up by nitric acid (20 c.c. of sp. gr. 1·33), and the solution diluted to about 400 c.c. with water. The siliceous gangue and lead sulphate are now collected on a double tared filter, and after being washed, dried, and weighed, the lead sulphate is extracted from the weighed precipitate by trituration in a glass mortar with hot sodium tartrate solution (20 per cent.). The siliceous gangue remains unchanged, and is again collected on the tared filters and weighed; the weight of lead is thus determined. The liquid containing the silver and zinc is now made up to a standard volume (500 c.c.); in part of this (50 c.c.), after separating the iron and aluminium by ammonia, the zinc is precipitated with ammonium hydrosulphide, and the precipitate collected and dissolved in hydrochloric acid; the solution after being filtered is precipitated hot with sodium carbonate, and the zinc weighed as oxide. The remaining liquid (450 c.c.), containing the silver, is rapidly evaporated to 20—30 c.c. and cooled, the clear solution is decanted from the

crystalline deposit, and pure sodium chloride (1 gram) added to it to precipitate the silver as chloride; this is then collected, dried, and weighed on a double tared filter. W. J. P.

Essence of Sandal Wood. By E. Mesnard (*Compt. rend.*, **114**, 1546—1547).—Adulteration of essence of sandal wood with terebenthene, oil of cedar, oil of cubebs, copaiva, &c., is detected by mixing it with concentrated sulphuric acid. When the essence is pure, the mixture is at first viscous, then becomes pasty, and very rapidly changes to a pale bluish-grey or greyish, solid mass which adheres strongly to glass; when impure, the viscous mixture does not completely solidify, has a dark colour and a very distinct lustre. If 2 to 3 centigrams of the essence is mixed with a drop of strong sulphuric acid and poured on a ground glass plate, and the end of a small glass rod attached to the under side of a balance pan is inserted in the viscous mixture, the degree of adherence of the solidified mass can be measured, and the amount of adulteration roughly estimated. C. H. B.

Detection of Higher Alcohols in Spirits of Wine. By C. Bardy (*Compt. rend.*, **114**, 1201—1204).—A preliminary examination is made by agitating 10 c.c. of the alcohol with 100 c.c. of a saturated salt solution. If an oily upper layer does not separate, 100 c.c. of the alcohol is agitated with 450 c.c. of a saturated salt solution in a vessel provided with a stop-cock; sufficient water is added to redissolve the salt that is precipitated, and then 60 to 70 c.c. of carbon bisulphide, and the mixture is well agitated. After a short time, the bisulphide is transferred to a smaller similar vessel, and the extraction is repeated a second and third time with similar quantities of carbon bisulphide, the whole of the latter being transferred to the second vessel. In order to separate the alcohols from the bisulphide, the latter is mixed with sufficient concentrated sulphuric acid (about 2 c.c.) to form a heavier layer at the bottom of the vessel, and, after vigorous agitation, the acid is transferred to a smaller vessel. The extraction is repeated several times with 1 c.c. of acid each time, and the various quantities of acid are mixed, heated at 50—60°, and a current of air passed over the surface of the liquid until all the bisulphide is expelled. An equal volume of glacial acetic acid is then added, and the mixture heated on a water-bath at about 100° for a quarter of an hour, the flask being fitted with a reflux condenser. When the action is complete, the contents of the flask are poured into 100 c.c. of saturated salt solution. If higher alcohols were originally present, the corresponding acetates separate and form an upper layer, the volume of which can be measured by any of the usual methods, the liquid being previously cooled to 15°. The number of cubic centimetres of acetates multiplied by 0·8 gives the percentage of higher alcohols in the alcohol examined.

If in the preliminary test an oily upper layer separates, only 25 c.c. of the alcohol should be taken and mixed with 100 c.c. of saturated salt solution and 8 to 10 c.c. of water. The quantity of carbon bisulphide, however, ought not to be reduced, and all the other operations are conducted in the manner described.

The carbon bisulphide dissolves only butyl and amyl alcohols, and if propyl alcohol is sought for, the salt solution that has been extracted with bisulphide is filtered and distilled until an alcoholometer in the receiver marks 50°. The quantity of propyl alcohol in the distillate is estimated by titration with permanganate (Barbet) or by Gossart's method.

Alcohol in the distillery residues known as "essential oils" may be determined by a modification of this method. 500 c.c. is agitated with an equal volume of salt solution, and the latter is extracted with three successive quantities of carbon bisulphide and afterwards distilled. The alcoholic strength of the distillate, corrected, if necessary, for the presence of propyl alcohol and calculated to the original volume, gives the percentage of alcohol present.

This method will detect 0·5 per cent. of higher alcohols in spirits of wine. Greater sensitiveness can be obtained by working with a larger quantity of the alcohol, but in this case a correction must be made on account of the ethyl acetate formed from the alcohol dissolved by the carbon bisulphide. C. H. B.

Reactions of Amidobenzoic Acids. By O. de Coninck (*Compt. rend.*, **114**, 1275—1276).—Orthoamidobenzoic acid, when heated with a slight excess of pure potassium nitrite, yields a substance that forms a garnet-red solution in dilute alcohol. The para- and meta-acids form compounds which yield orange-red solutions.

When heated to fusion with a slight excess of ammonium nitrate, the acids form two layers, the lower pale red and the upper violet. With a smaller proportion of the salt, a deep coloration is formed, sometimes red, sometimes brown, and if the substance is cooled for a short time and mixed with a little water, a colourless solution is formed which regains the original colour on heating.

Uranium nitrate, on heating gently, yields a sublimate which is bright red with the ortho-derivative, and forms an amber-yellow alcoholic solution; brown with the meta-acid, and forms a red-brown alcoholic solution; orange with the para-acid, and forms a deep-yellow alcoholic solution.

Bleaching powder, when heated gently with the ortho-acid, yields a deep-violet magma, forming a red solution with concentrated alcohol, which after a time shows a violet fluorescence. The para- and meta-acids also yield red solutions under the same conditions, but they show no fluorescence.

Zinc chloride heated just to fusion gives an amber-coloured mass with the ortho-acid, deep violet with the meta- and para-acids.

Stannous chloride on heating gives yellow products with all three acids.

Stannic chloride acts energetically on the ortho-acid. The solution of the product in dilute alcohol is red. The meta- and para-acids give no reaction, except that sometimes the meta-acid yields a small quantity of violet sublimate. C. H. B.

General and Physical Chemistry.

Hasselberg's so-called Second or Compound Hydrogen Spectrum and the Structure of Hydrogen. By A. Grünwald (*Monatsh.*, **13**, 111—244).—Balmer showed that the wave-lengths of a portion of the rays in the line spectrum of hydrogen, emitted at high temperature, are in simple rhythmical relation one to another. At low pressures and temperatures, hydrogen emits not only the above rays, but a number of other relatively weaker ones, forming the so-called second or compound line spectrum, which has been specially described by Hasselberg. The lines in this second spectrum do not appear at first sight to bear any relations one to another, but the author, who has been engaged in a very complete and lengthy investigation of this point, finds that certain regularities do exist.

The lines in the second hydrogen spectrum may be divided into groups G_1, G_2, G_3, ..., G_n in such a manner that each line in one group corresponds with a line in each of the other groups. The reciprocal value of the wave-lengths of homologous lines $1/\lambda_1$, $1/\lambda_2$, $1/\lambda_3$, ..., $1/\lambda_n$ are found to be in the proportions to one another of the numbers $1 - \frac{4}{3^2}$, $1 - \frac{4}{4^2}$, $1 - \frac{4}{5^2}$, ..., $1 - \frac{4}{(n+2)^2}$. Of these groups there would appear to be at least 14, there being a necessary limit to their number as there is to that of the particles which transfer these different vibrations to the ether. H. C.

Theory of Secondary Batteries. By F. Streintz (*Ann. Phys. Chem.* [2], **46**, 449—463).—The author proves by measurements of the E.M.F. the presence of hydrated peroxide of lead as a secondary product on the plates of secondary elements, and considers that its formation is accompanied by a diminution of the E.M.F. of the element on charging, and its destruction by a corresponding increase on discharging.

Experiments were made to ascertain the dependence of the E.M.F. on the concentration of the acid in the cells. If the E.M.F. (E) is expressed in volts and the strength of acid (z) in grams H_2SO_4 per litre of solution, the following relation holds good for the ordinary temperature:—

$$E_z = 1{\cdot}850 + 0{\cdot}00057z,$$

or if s is the specific gravity of the solution and s_0 that of water at the temperature of experiment, then

$$E_s = 1{\cdot}850 + 0{\cdot}917\,(s - s_0).$$

The temperature coefficient of the E.M.F. was always found to be positive. Measurements were made at every fifth degree between 10° and 70°. The following are the coefficients for various values of the E.M.F:—

E.	$\frac{dE}{dT}10^6$.	
1·9223	140	
1·9828	228	
2·0031	335	
2·0084	285	
2·0105	255	
2·0779	130	
2·2070	73	J. W.

Alteration of the Conductivity of a Solution by the Addition of a Small Quantity of a Non-Electrolyte. By R. J. Holland (*Ber.*, **25**, 2726—2727).—The author's work differs from that of Arrhenius (this vol., p. 1038) in that the non-electrolytes employed (benzene, toluene, xylene, and turpentine oil) were none of them solvents of the salts examined; purified methyl alcohol, dried by distillation with anhydrous copper sulphate, was the solvent used, solutions of 1/100, 1/1000, and 1/2000 normal concentrations being investigated with successive additions of 5, 10, 15, and 20 per cent. by volume of the non-electrolyte. The following are the general results with lithium, sodium, and potassium nitrate:—(1) The reduction of the conductivity by the addition of a non-electrolyte is proportional to the amount of the latter added; (2) the reduction of the conductivity varies according to the nature of the dissolved salt and that of the non-electrolyte; (3) the graphic representations of the molecular conductivities are straight lines. A. R. L.

Expansion of Water by Heat. By C. Puschl (*Monatsh.*, **13**, 440—449).—The author discusses the effect of pressure on the expansion by heat of water. Making use of Amagat's determinations, he shows that at high pressures (3000 atmos.) the expansion for each degree of temperature reaches a maximum as the temperature rises, and then begins to fall. H. C.

Stochiometry of Solutions. By G. Jäger (*Monatsh.*, **13**, 483—497).—In a former paper, the author has shown that the heat of vaporisation of a solution

$$r' = r[1 + (\kappa - \lambda)q] = r\left[1 + \frac{b\kappa}{r}\,q\right],$$

where r is the heat of vaporisation of the solvent, q the number of gram-molecules of dissolved substance in 1 litre of the solution, κ and λ constants, and b that portion of the heat of vaporisation which is necessary to overcome capillary forces. It is here shown that r' is also equal to $r + 2\mathrm{A}v(d - d')$ where A is the mechanical equivalent of heat, d and d' the vapour pressure of the pure solvent and the solution, and v the volume of the solution. A number of interesting relationships are thus established between various properties of solutions.

It is also shown that the heat of fusion of a solution is smaller than that of the pure solvent, the difference being proportional to

the number of molecules of dissolved substance present in unit volume of the solvent. H. C.

Heat of Formation of Permolybdic Acid. By E. Péchard (*Compt. rend.*, **115**, 227—229).—The direct neutralisation of permolybdic acid by sodium hydroxide develops +24·2 Cal., and by potassium hydroxide +24·0 Cal. The action of sulphuric acid on sodium permolybdate develops +6·9 Cal., and the result is the same whether the sulphuric acid is added all at once or in successive portions. The whole of the molybdic acid is not displaced, but a very acid molybdate is formed, its formation corresponding with 0·6 Cal.

The action of hydrogen peroxide on a mixture of sodium molybdate with sulphuric acid in molecular proportion develops +5·4 Cal., a quantity which may be regarded as the sum of the heat developed by the decomposition of the hydrogen peroxide and that absorbed by the formation of the permolybdate. It follows that the formation of the permolybdate absorbs −16·2 Cal.

The direct neutralisation of permolybdic acid develops with sodium hydroxide +11·2 Cal., and with potassium hydroxide +11·1 Cal. It follows that permolybdic acid will displace carbonic acid, but is itself displaced by the strong acids. The action of alkaline hydroxides on the permolybdates, with production of molybdates, gives for the heat of formation of permolybdic acid from molybdic acid −15·9 Cal., a number almost identical with that obtained by the action of hydrogen peroxide. The energy necessary for the formation of the permolybdic acid is derived from the decomposition of the hydrogen peroxide. C. H. B.

Molecular Volumes of Dissolved Substances. By J. Traube (*Ber.*, **25**, 2524—2533).—The author has compared the molecular volumes of a large number of salts in aqueous solution as found by different investigators with the degree of electrolytic dissociation or "ionisation" of the salts, and finds that a very close relation exists between the two (compare Schmidt, Abstr., 1890, 844). To the objection of Ostwald that the numbers cannot simply represent molecular volumes of the dissolved substances, inasmuch as they are in certain cases negative, the author replies that in all such cases the salts contain water of crystallisation, and that when allowance is made for the contraction of the latter, the negative value disappears, and numbers are obtained which correspond with those of the anhydrous salts. H. G. C.

Permeability of Precipitated Membranes. By G. Tammann (*Zeit. physikal. Chem.*, **10**, 255—264).—Traube was of opinion that precipitated membranes were of the nature of molecular sieves, which let small molecules pass through them, but stopped large molecules. Ostwald (Abstr., 1890, 1354) developed this idea of Traube's for salts, and stated that membranes might be permeable, not for salt molecules as such, but for particular ions. Salts, of which both ions

could pass the membrane, would pass through as a whole; whilst if one of the ions were stopped, the salt could not pass at all.

The author has put these ideas to experimental proof. First of all, he took three membranes (tannate of gelatin, zinc ferrocyanide, and copper ferrocyanide) and determined their permeability to 17 different dye-stuffs (salts and acids) in aqueous solution. If the molecular sieve theory is correct, the order of permeability of the three membranes ought to be the same for all the dissolved substances. This he found not to be the case.

Acids diffuse through membranes of copper ferrocyanide in the order of their strength, that is, of their degree of dissociation into ions. This would indicate that it is principally the ions which pass the membrane, and not the undissociated acid. The following are some of the numbers obtained:—

Hydrochloric acid	9·0
Trichloracetic acid	6·6
Monochloracetic acid	3·3
Acetic acid	2·6

Experiments were made with a large number of salt solutions in respect of their power to pass through different membranes. The chlorides, bromides, and nitrates of potassium, ammonium, sodium, and lithium pass easily through copper ferrocyanide membranes. The corresponding sulphates diffuse with greater difficulty. The membrane is impervious to calcium and magnesium salts, but allows chlorides and bromides of barium and strontium to pass. Succinic, tartaric, citric, and isobutyric acids penetrate the membrane, but their potassium salts do not. These examples are sufficient to show that Traube's and Ostwald's views are untenable without modification.

The author inclines to the opinion that the process of passage through the membrane may be one of solution, as all the semi-permeable membranes with which we are acquainted are strongly hydrated. J. W.

Solubility Curves of Pairs of Salts. By H. W. B. Roozeboom (*Zeit. physikal. Chem.*, **10**, 145—164).—In this paper, the author discusses the solubility relations of pairs of salts which are capable of forming a double salt with each other as well as mixed crystals, and has examined in particular the solubility in water of mixtures containing ferric chloride and ammonium chloride in various proportions (compare this vol., p. 1048). He tabulates his results so that the numbers of molecules of ammonium chloride dissolved from the mixtures by 100 mols. of water appear as abscissæ, and the corresponding numbers for ferric chloride as ordinates. The solubility of the pair $Fe_2Cl_6 : NH_4Cl$ at 15° is expressed in this way by an isotherm which consists of three curves cutting in pairs.

The first curve is for solutions which are in equilibrium with the hydrate $Fe_2Cl_6,12H_2O$, and runs between the limits

$$\left.\begin{matrix} 9{\cdot}30 \text{ to } 9{\cdot}93 \text{ mols. } FeCl_3 \\ \text{and} \quad 0 \text{ to } 1{\cdot}36 \text{ mols. } NH_4Cl \end{matrix}\right\} \text{to 100 mols. } H_2O.$$

The second curve gives the composition of the solutions in equilibrium with the double salt $4NH_4Cl,Fe_2Cl_6,2H_2O$.

Its limits are—

$$\left.\begin{array}{l} 9{\cdot}93 \text{ to } 6{\cdot}8 \text{ mols. } FeCl_3 \\ \text{and } 1{\cdot}36 \text{ to } 7{\cdot}8 \text{ mols. } NH_4Cl \end{array}\right\} \text{to 100 mols. } H_2O.$$

The third curve is for solutions which can exist in presence of mixed crystals (containing from 7·3 down to 0 per cent. of ferric chloride). It runs between the limits

$$\left.\begin{array}{l} 6{\cdot}8 \text{ to } \quad 0 \text{ mols. } FeCl_3 \\ \text{and } 7{\cdot}8 \text{ to } 11{\cdot}88 \text{ mols. } NH_4Cl \end{array}\right\} \text{to 100 mols. } H_2O.$$

The solution at the point of intersection of the two first curves is stable in presence of the hydrated ferric chloride and the double salt: that at the intersection of the second and third curves can exist in presence of the double salt and the mixed crystals containing the maximum amount of iron. The composition of the solutions at these points is independent of the quantity of the two solid phases. Whilst, however, the solution at the first intersection is not further altered by any addition of ferric chloride, or by the addition of ammonium chloride up to the point where all the solid ferric chloride is converted into the double salt, the solution at the second intersection is changed by the addition of one or other component, for each of these transforms one solid phase into the other.

The curve for the double salt shows that this salt cannot be dissolved without undergoing decomposition.

The mixed crystals contain the ferric chloride as Fe_2Cl_6 with 7 to 8 mols. H_2O; but whether as an isotropic or æolotropic admixture remains undecided. The relation between the quantity of iron in the mixed crystals and that in the solution is not well known.

The author enumerates various cases of solubility isotherms for salt pairs of different types. These all consist of one or more curves cutting each other in pairs. He also shows for these cases how the mixed solutions are changed by the addition of one or other solid component. J. W.

Solubility of Double Compounds. (Part II.) By R. Behrend (*Zeit. physikal. Chem.*, **10**, 265—283; compare this vol., p. 1047).—In this paper, the solubility relations of the compound which phenanthrene forms with picric acid are investigated for alcoholic solutions. The method was to dissolve the picrate (alone or with excess of phenanthrene or of picric acid) in warm, absolute alcohol, allow it to remain for a week at the ordinary temperature, kept constant as far as possible, and then estimate what had remained in solution as follows:—A weighed quantity of the solution was taken, and the alcohol driven off by a current of air at 60°. The residue was weighed, the picric acid in it determined by titration, and the phenanthrene by difference.

The results show that the picrate in saturated alcoholic solution at 12° is decomposed to the extent of almost 90 per cent. Considerable divergencies from the calculated numbers appear when a large excess

of phenanthrene is added. These the author shows to be due to the formation of complex (probably triple) molecules of phenanthrene in concentrated alcoholic solution. This conclusion is confirmed by observations of the boiling points of alcoholic anthracene solutions. In a 12 per cent. solution, the molecular weight is found to be 27 per cent. too high.

The author recalculates some of Beckmann's numbers for the molecular weights of substances in alcoholic solution on various assumptions as to the nature of the complex molecules formed. J. W.

Transportation of Solids in a Vacuum by the Vapours of Metals. By H. N. Morse and J. White, Jun. (*Amer. Chem. J.*, **14**, 314—315; compare Abstr., 1889, 775; 1891, 643).—The action is merely mechanical; barium carbonate and powdered porcelain are transported with equal facility and without change of composition, and porous plugs of asbestos allow the metallic vapours to pass, but stop all the solids. The explanation advanced previously by the authors, ascribing the result to dissociation, was erroneous.

The authors have also re-examined the gas given off on heating the oxides of zinc, cadmium, and magnesium in a vacuum with their respective metals. It is found to be pure nitric oxide, and is derived from some nitrate present in the oxide used. W. T.

Bunsen Burner for Spirit. By G. Barthel (*Ber.*, **25**, 2646—2648).—The burner consists of a thick-walled tube, fastened into an iron foot. The tube is divided horizontally into two parts. The lower part is filled with a metal network, and serves to vaporise the spirit. Just above the division are air holes, similar to those in an ordinary Bunsen burner. The spirit is introduced from a vessel about 1 metre above the burner, through a tube running into the foot of the burner, and the supply is regulated by a screw-tap just below the air-holes. A piece of wire gauze in the upper part of the tube causes the flame to burn steadily.

The temperature is higher than that obtained by an ordinary Bunsen burner. 1 litre of water can be heated from 15° to 100° in $7\frac{3}{4}$ minutes, with the consumption of 26 grams of spirit.

A drawing of the apparatus is given. E. C. R.

Simple Apparatus for Evaporating under Reduced Pressure. By C. Schulze and B. Tollens (*Annalen*, **271**, 46—48).—For the rapid evaporation of solutions of substances which readily undergo decomposition, the authors describe an apparatus similar in principle to that recently recommended by Yaryan for use in the extraction of sugar on the large scale.

The apparatus consists of a copper worm, immersed in boiling water, and closed at the top with an india-rubber cork through which passes a moderately wide glass tube; into the wide glass tube is fitted an india-rubber cork, through which passes a narrower glass tube provided with a stopcock, the uppermost portion of the narrow glass tube being bent at a right angle and connected with a glass tube which dips into a vesssl containing the solution to be evaporated.

The bottom of the copper worm is connected with one limb of a three-way, bulbed tube; of the other limbs, one passes directly downwards through an india-rubber cork into a closed flask-shaped vessel, whilst the other passes upwards, and, after bending over, is connected with a condenser. The lower end of the condenser fits air-tight into a flask which is connected with a water-pump, so that the whole of the apparatus is constantly exhausted. By opening the stopcock at the top of the copper worm, the solution to be evaporated is drawn into the apparatus, its flow being regulated at will; evaporation then takes place in the worm, the concentrated liquid falling into the flask-shaped receiver, whilst the water or other vapour passes onwards into the condenser. The flask-shaped receiver is provided with a lateral tubulus, closed with an india-rubber cork, through which passes a glass siphon tube; when a sufficient quantity of the concentrated solution has collected in the receiver, air is admitted into the apparatus, and the liquid is drawn off through the siphon.

F. S. K.

Inorganic Chemistry.

Compounds of Chlorine with Iodine. By W. Stortenbeker (*Zeit. physikal. Chem.*, **10**, 183—202).—Calorimetric observations on the chlorides of iodine, made by the author by means of a Berthelot calorimeter, lead to the following results:—

	Per gram.	Per gram-molecule.
Specific heat of liquid ICl	0·158	—
„ ICl_α (m. p. 27·2°).	0·083	—
„ ICl_β (m. p. 13·9°).	*ca.* 0·085	—
Heat of fusion of ICl_α	−16·42 cal.	−2658 cal.
„ ICl_β	−14·0 „	−2267 „
Heat of transformation of ICl_β into ICl_α	1·25 „	203 „

The depression of the freezing point of glacial acetic acid by the chlorides gives numbers corresponding with the formula ICl for the monochloride and $ICl_3/2$ for the trichloride. There may nevertheless be dissociation of the monochloride in solution into chlorine and iodine, for the number of molecules on the two sides of the equation $2ICl = I_2 + Cl_2$ is the same. The trichloride evidently dissociates in solution into $ICl + Cl_2$, the molecular depression decreasing as the concentration increases. These results agree with those obtained from vapour density determinations.

The author attempted other freezing point experiments by using the monochloride itself as solvent, the melting point of which is depressed by an excess of chlorine or excess of iodine. When there is excess of chlorine present, the solution very probably contains tri-

chloride. But as the trichloride tends to dissociate into monochloride and chlorine, we have here a case in which the solvent is one of the dissociation products of the dissolved substance. Raoult's law does not apply directly to such a case. The author discusses the subject from the thermodynamical point of view, and develops the necessary equations. J. W.

Iodine Trichloride. By E. Tavel and A. Tschirch (*Arch. Pharm.*, **230**, 331—341).—Iodine trichloride is decomposed by water with formation of the monochloride, hydrogen chloride, and iodic acid. It is thus a matter of indifference whether the trichloride or the monochloride be employed as an antiseptic. The action of the trichloride (that is, the monochloride) solution on *Staphylococcus citreus*, green pus, and the anthrax bacillus is very energetic, rivalling that of chlorine. The hydrochloric and iodic acids play only a subsidiary part; the antiseptic action of the latter is stronger than that of the former for *Staphylococcus citreus* and green pus.

A. G. B.

Iodic Acid and its Salts. By A. Ditte (*Ann. Chim. Phys.* [6], **21**, 145—188).—The author describes the preparation and properties of the iodates of most of the common metals, and of a number of organic bases. Many of the metallic salts have been previously described by Rammelsberg, Millon, Marignac, and others; the organic salts crystallise readily. F. S. K.

Atomic Weight of Oxygen. By A. Leduc (*Compt. rend.*, **115**, 311—313).—The calculations are based entirely on the sp. gr. of electrolytic gas, hydrogen, and oxygen (compare Abstr., 1891, 1416). Special precautions were taken to ensure the purity of the electrolytic gas, which was made by passing a current of 5 ampères between platinum electrodes in 30 per cent. aqueous potash for several days under constant conditions of temperature and pressure.

The sp. gr. of electrolytic gas referred to air was thus found to be 0·41423; with a maximum error of 1 in 10,000. Taking the sp. gr. of hydrogen as 0·06947, and that of oxygen as 1·10503, electrolytic gas contains 66·708 per cent. of hydrogen and 33·292 per cent. of oxygen by volume, so that the ratio of hydrogen to oxygen is 2·0037, and the atomic volume of oxygen 1·9963. The atomic weight of oxygen calculated from these data

$$\left(= \frac{\text{vol. per cent. of oxygen} \times \text{sp. gr. of oxygen}}{\text{vol. per cent. of hydrogen} \times \text{sp. gr of hydrogen}}\right)$$

is 15·877, a number agreeing closely with the value 15·882 previously obtained by the author by a synthetical method (this vol., p. 1271). The value 15·88 is considered the most probable. The molecular weight of water vapour is then 17·88, giving a sp. gr. of 0·6212, taking that of hydrogen as a basis, or 0·6221, taking that of oxygen as a basis. The latter is probably the more correct, as the compressibility of oxygen is approximately equal to that of air.

Jn. W.

Insoluble Sulphur. By W. Schmitz-Dumont (*Ber.*, **25**, 2659—2661).—Bellamy (*Compt. rend.*, **91**, 330) has stated that sulphur insoluble in carbon bisulphide differs from the soluble modification in the following particulars :—If sodium thiosulphate is being prepared from the neutral sulphite and the insoluble modification of sulphur, then : (1) hydrogen sulphide is formed during the boiling ; (2) the hot filtered solution becomes milky after a time, and a notable quantity of sulphur separates out with the thiosulphate ; (3) the insoluble modification is dissolved in greater quantity than the soluble modification.

The author, however, was unable to detect any difference in chemical behaviour between the soluble and insoluble modifications. Quantitative experiments showed that both modifications evolve the same amount of hydrogen sulphide when boiled with sodium sulphite, and also when boiled with water. On crystallising the thiosulphate, no precipitation of sulphur was observed, and on allowing the solution to remain, it gradually became milky, just as a solution of hydrogen sulphide does. Also both modifications are equally soluble in the sulphite ; but the insoluble modification dissolves somewhat more quickly. E. C. R.

Formation of Sulphuric Acid and Ammonium Sulphate by Burning Coal Gas. By E. Přiwoznik (*Ber.*, **25**, 2676—2680).—From the following experiments, the author concludes that free sulphuric acid is not given off by burning coal gas. If a platinum dish containing about 0·5 litre of water is placed over a Bunsen flame so that only the point of the flame is in contact with the dish, the cold dish becomes covered with dew, which gradually disappears without leaving a deposit of sulphuric acid. After heating for half an hour, a small deposit of ammonium sulphate is formed. Again, if 5 litres of water free from ammonia is evaporated to a small bulk in a platinum dish over a Bunsen flame, and the residue then evaporated to dryness on the water-bath, a dry salt is obtained, which would not be the case if the liquid contained free sulphuric acid. When vessels of porcelain or enamelled iron are employed instead of platinum, ammonium sulphate is also formed, but the formation of a dew of sulphuric acid could not be detected.

The author suggests that the formation of sulphuric acid, so often noticed when platinum is employed, is due to the combination of sulphurous acid with oxygen condensed on the platinum. Thus, if a platinum dish heated to redness by means of a spirit lamp is held over a porcelain basin containing sulphurous acid, sulphuric acid is formed and may be detected by rinsing the platinum dish with water, acidifying the solution with hydrochloric acid, and adding barium chloride. E. C. R.

The Amides and Imides of Sulphuric Acid. By W. Traube (*Ber.*, **25**, 2472—2475).—If a solution of sulphuryl chloride in 15 to 20 times its volume of chloroform is saturated with dry ammonia, the product shaken with water until the precipitate has dissolved, and the aqueous solution boiled with lead or silver oxide until all

chlorine is removed, the filtered solution, when evaporated, leaves a viscid, hygroscopic syrup; this gives no precipitate with barium or platinum chloride, but is converted into ammonium sulphate by boiling with hydrochloric acid. It is possibly the neutral amide of sulphuric acid, $SO_2(NH_2)_2$; with mercuric nitrate, lead acetate, or ammoniacal silver nitrate, it gives precipitates from which hydrogen sulphide liberates the original substance. When heated, it loses ammonia; at a higher temperature, sulphurous anhydride is evolved. If the silver compound is heated (better with a little ammonium chloride) at 170—180° until no more ammonia is evolved, the silver salt of sulphimide, SO_2NAg, is formed; it crystallises from very dilute nitric acid in long needles, and dissolves readily in hot, sparingly in cold water. Its solution gives no precipitate with barium nitrate, even after the silver has been removed by means of hydrochloric acid. When heated, it leaves metallic silver, mixed with a little silver sulphate. C. F. B.

Action of Nitric Peroxide on Metals and Metallic Oxides; Nitro-metals. By P. Sabatier and J. B. Senderens (*Compt. rend.*, **115**, 236—239).—Nitric peroxide acts more readily than nitric oxide on metals and metallic oxides, and usually yields more highly oxidised products.

Manganous oxide at about 350° yields the sesquioxide; titanium sesquioxide at 300° yields titanic anhydride; brown tungsten dioxide becomes incandescent at 300°, and yields tungstic anhydride; black vanadium trioxide oxidises between 300° and 400°, and yields the brownish yellow pentoxide; cuprous oxide at 300° yields cupric oxide.

Aluminium foil is not appreciably oxidised at 500°; magnesium foil is oxidised only at a dull red heat, but at this temperature it burns with great energy; zinc oxidises regularly at 300°; lead oxidises slowly at 200°, and yields a white basic nitrate. Reduced iron oxidises with incandescence at about 350°, and yields ferric oxide; reduced cobalt burns brilliantly at the ordinary temperature, and yields the black oxide, Co_3O_5; reduced copper at 250° yields cupric oxide.

Nitro-metals.—Reduced copper absorbs nitric peroxide at the ordinary temperature with considerable development of heat, the mass becoming perceptibly warm, and when this development of heat ceases, a maroon-coloured product is obtained of the composition Cu_2NO_2. This compound reacts violently with water, and yields pure nitric oxide, a solution of cupric nitrate with a small quantity of nitrite, and a residue of metallic copper. When heated in pure and dry nitrogen, nitric peroxide is evolved, and a residue of partially oxidised copper is left. In the preparation of this compound, the nitric peroxide must be quite free from nitric acid, and this is secured by placing in the front part of the tube a layer of litharge followed by a layer of phosphoric anhydride.

If a current of nitric peroxide largely diluted with nitrogen is passed over reduced cobalt, the latter does not burn, but yields a black *nitro-cobalt*, Co_2NO_2, very similar in properties to the copper compound. C. H. B.

Hydroxylamine. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **11**, 18—49; compare this vol., p. 402).—Hydroxylamine hydrochloride dissolved in methyl alcohol is treated with sodium methoxide as previously described, and the greater portion of the alcohol, after separation of the sodium chloride, is distilled off at a pressure of 100 mm.; the residue is further distilled in small portions at a time under a pressure of 40 mm. as rapidly as possible, frothing being prevented by the addition of a little vaseline. So soon as solid hydroxylamine passes over, the receiver is changed for one cooled in iced water, especial care being taken to avoid contact of hydroxylamine with the air for any length of time at 60—70°, since under these circumstances it explodes violently. The crystalline hydroxylamine may be further purified by fractional crystallisation. From 1·2 kilos. of hydroxylamine hydrochloride, the author obtained 100 grams of crystalline hydroxylamine.

Solid hydroxylamine forms white, inodorous scales or hard needles, which melt at about 33·05°, but remain in a state of superfusion on cooling to 0°; it boils at 58°under a pressure of 22 mm.; when heated at 90—100°, it decomposes with evolution of gas, and detonates at a higher temperature. The crystals have a sp. gr. of 1·35 as determined by the method of suspension, using a mixture of chloroform and benzene; whilst in the liquid state, as taken by Westphal's balance and the pyknometer, the value 1·23 is obtained. Eykman determined the refractive index at 14° and 40° respectively as n_a = 1·44123 and 1·43359. Hydroxylamine may be titrated, using methyl-orange as an indicator. An elementary analysis by Dumas' method and determination of its molecular weight by Raoult's method indicate a molecular weight of 33. On exposure to air, the crystals liquefy, increase in weight, and volatilise completely. The pure substance is stable, but the presence of traces of free alkali, as in some glass bottles, causes it to decompose, and it is slowly oxidised on exposure to air, but the concentrated solutions are very stable. Heated at 90°, decomposition occurs, the temperature rises to 130°, and a violent explosion ensues, but at 40—45° it may be decanted without risk. In addition to the properties previously described (*loc. cit.*), methyl alcohol at 5° dissolves 35 per cent.; ethyl alcohol at 15°, 15 per cent.; and boiling dry ether 1·2 per cent., the latter solution depositing acicular crystals on cooling; ethyl acetate dissolves 1·6 per cent.

Hydroxylamine inflames in a current of dry chlorine; bromine and iodine, however, decompose it without flame, with formation of hydrobromic and hydriodic acids. Exposed to the air, solid hydroxylamine suffers oxidation; a white deposit is formed which contains both nitrous acid and ammonia, and when dry oxygen is passed through fused hydroxylamine, white fumes of nitrous acid are produced with but little liberation of heat. Sodium attacks hydroxylamine with production of flame, and when added to its solution in dry ether, hydrogen is evolved, and a voluminous, white, amorphous substance is formed; on exposure to air, this liquefies, develops heat, and intumesces with evolution of gas and formation of nitrous acid. A quantitative research on this reaction tends to the belief that a compound of hydroxylamine with sodium hydroxylaminate is formed, and that this

compound explodes spontaneously. Sulphur, phosphorus, and magnesium powder do not react with hydroxylamine, but warm zinc-dust reduces it with formation of ammonia and zinc oxide, an explosion occurring if notable quantities are involved.

Crystals of potassium permanganate, chromic acid, ammonium dichromate, potassium and sodium chromates placed in contact with hydroxylamine crystals produce decomposition with a white flame, but potassium and sodium dichromates cause a sharp, violent explosion.

The oxides and peroxides of the metals also induce decomposition, with production of flame, as do potassium chlorate, perchlorate, and bromate on the addition of a drop of sulphuric acid. Iodic anhydride attacks hydroxylamine when the latter is not in excess, with liberation of iodine, and hydroxylamine reduces sodium iodate to iodide, the reaction in each case being violent. Powdered silver nitrate is reduced by hydroxylamine to the metallic condition, and anhydrous cobalt sulphate to a brown, amorphous mass. Anhydrous copper sulphate inflames hydroxylamine, and the powdered hydrated salt is reduced, but the anhydrous sulphates of nickel, manganese, magnesium, and zinc are unaffected.

Hydroxylamine dissolves sodium and barium hydroxides, and a solution of the first named substance absorbs oxygen from the air with formation of nitrous acid, becoming gradually warmer and entering into a state of effervescence with evolution of steam and ammonia. Hydroxylamine reacts with hydrogen peroxide to form nitrous acid, and a strong solution of sodium hypobromite rapidly oxidises it. Phosphorus trichloride and pentachloride cause the ignition of hydroxylamine, and the addition of a chloroform solution of the trichloride to solid hydroxylamine suspended in that solvent, causes the formation of a voluminous, white, amorphous mass, which contains phosphorous acid, hydroxylamine, and chlorine.

Rapid currents of carbonic anhydride and carbonic oxide, of nitrous oxide, and of nitric oxide are without effect on melted hydroxylamine, but nitric peroxide is reduced thereby. Hydroxylamine dissolves gaseous ammonia freely, also carbonic anhydride and hydrogen sulphide, forming with the last two, thick liquids which do not solidify at $-10°$. Benzyl chloride, methyl iodide, and acetone react eagerly with hydroxylamine; the dinitrobenzenes are attacked, but nitrobenzene is not. A solution of hydroxylamine in methyl alcohol reduces silver nitrate, and forms a bluish violet precipitate with anhydrous copper sulphate dissolved in that solvent.

Together with Crismer (Abstr., 1890, 558), the author has mentioned the fact that hydroxylamine forms with some chlorides compounds analogous to their hydrated salts. In the present paper, he gives determinations of the solubilities of some salts and of ammonia in hydroxylamine.

In concluding, he discusses the validity of the formulæ proposed for hydroxylamine, and decides in favour of $NH_2{\cdot}OH$. T. G. N.

Boron Trisulphide. By H. Moissan (*Compt. rend.*, **115**, 203—208).—Boron trisulphide can be obtained in several ways:—(1.) By

the action of melted sulphur on boron iodide; even after heating at 240°, the product retains a small quantity of sulphur. (2.) By the action of sulphur vapour on amorphous boron; at 610° the boron becomes covered with a protecting layer of the sulphide, but at 1200°, if a very slow current of hydrogen is passed through the tube with the sulphur vapour, the boron sulphide sublimes. The product is yellow, and has a crystalline fracture, but contains a large excess of sulphur, the greater part, but not all, of which can be removed by distillation. This retention of sulphur is due to the existence of a boron pentasulphide. (3.) By the action of hydrogen sulphide on pure boron at a bright red heat; the product is crystalline, white, and very light, and is decomposed by water without any separation of sulphur. (4.) By the action of pure carbon bisulphide vapour on boron at a bright red heat; the product is white and crystalline. (5.) By the action of tin, antimony, or arsenic sulphide on amorphous boron at a red heat.

When condensed in a large receiver, boron sulphide forms white, slender needles, which are very unstable, and are decomposed by water with evolution of hydrogen sulphide and without separation of sulphur. It begins to melt at 310°, and passes through a pasty condition; sp. gr. about 1·55. It is insoluble in most solvents, but is slightly soluble in phosphorus trichloride, from which it crystallises in slender, colourless needles, and is still more soluble in sulphur chloride, from which it does not crystallise, probably in consequence of the formation of a new compound.

Hydrogen does not reduce boron sulphide between a dull red and a bright red heat. When thrown into chlorine, the sulphide burns with a green flame, forming boron and sulphur chlorides, and in presence of excess of chlorine these compounds yield a double compound of boron trichloride and sulphur tetrachloride, liquid at the ordinary temperature but solid at −23°. Bromine has no action on the sulphide at the ordinary temperature, but on heating, an energetic reaction takes place. Iodine has no reaction even at the softening point of glass. At a dull red heat in a current of oxygen, boron sulphide burns with a green flame, but the layer of oxide formed prevents the reaction from becoming complete. Sulphur dissolves in all proportions in fused boron sulphide, and cannot afterwards be entirely expelled by distillation. Nitrogen, phosphorus, carbon, and silicon are without action on the sulphide at a red heat, but sodium and potassium decompose it below dull redness with vivid incandescence, metallic sulphides and borides being formed. Magnesium behaves similarly, and yields magnesium sulphide and boron, but aluminium yields aluminium sulphide and aluminium boride. Reduced iron or silver, zinc, copper, or mercury gives no similar reaction.

Water decomposes boron trisulphide violently, and the reaction is expressed by Sabatier's equation, $B_2S_3 + 6H_2O = 2B(OH)_3 + 3H_2S$. Dry ammonia combines with boron sulphide with great development of heat, forming a yellow powder; this when heated yields a white residue which evolves ammonia on being treated with potassium hydroxide solution.

Boron trisulphide in nitric oxide at a red heat yields boric anhydride

and sulphur; in nitrogen peroxide, it yields boric anhydride and sulphuric anhydride. When thrown into nitric acid, oxidation takes place with incandescence. Bromine water converts it into boric and sulphuric acids. Hydrogen chloride at about 400° yields boron chloride and hydrogen sulphide; hydrogen iodide has no action even at 920°. Phosphorus, arsenic, and sulphur chlorides seem to form double compounds.

Organic compounds react energetically with boron sulphide, and, as a rule, yield hydrogen sulphide. Saturated hydrocarbons are without action. Terebenthene and amylene dissolve the sulphide in the cold with evolution of hydrogen sulphide. Methyl, ethyl, isobutyl, and amyl alcohols and the principal phenols behave similarly, and dissolve boron sulphide with evolution of hydrogen and without separation of sulphur. Acetic chloride at the ordinary temperature yields a volatile compound with a repulsive odour. Organic bases, and aniline in particular, form crystalline compounds with the sulphide at the ordinary temperature. Aldehydes also form crystalline compounds. Phenyl cyanide forms a crystalline compound which does not evolve hydrogen sulphide unless heated. C. H. B.

Boron Pentasulphide. By H. Moissan (*Compt. rend.*, **115**, 271—273).—*Boron pentasulphide*, B_2S_5, is a light, white, crystalline powder, which melts sharply at 390°, and has the sp. gr. 1·85. It is made by heating boron iodide (20 grams) with sulphur (rather less than 1 equiv.) in carbon bisulphide solution for 24 hours at 60°. The precipitated product is washed with carbon bisulphide to remove the iodine, but cannot be obtained in the pure state, as it forms a very sparingly soluble additive compound with the latter.

The pentasulphide is hydrolysed by water into boric acid, hydrogen sulphide, and sulphur, and resembles the trisulphide (preceding abstract) in its behaviour with alcohol, the excess of sulphur separating in the free state. It dissociates into the trisulphide and sulphur when heated to its melting point in a vacuum, and is decomposed in a similar manner when heated with mercury or silver, a sulphide of the metal being formed. It is converted by aqueous potash into potassium borate and polysulphide, and is acted on by chlorine at a low temperature with the formation of an unstable crystalline substance. Jn. W.

Artificial Corrosion of the Diamond. By W. Luzi (*Ber.*, **25**, 2470—2472).—Diamonds were corroded by heating them for half an hour in the melted matrix ("blue ground") in which they occur in South Africa. They were then found to have irregular or elliptical hollows on the surface, in one case so deep that the diamond was nearly bored through. At the same time the diamonds were usually blackened or covered with a red layer of iron oxide, and occasionally tiny black or dark-grey magnetic globules were observed in the hollows; these dissolved partly in hydrochloric acid with evolution of gas. Probably the process depends on a reduction of the magma at the expense of the carbon of the diamond. C. F. B.

Extraction of Rubidium and Cæsium Compounds from Carnallite. By W. Feit and K. Kubierschky (*Chem. Zeit.*, **16**, 335—339).—The authors' object was to obtain the rubidium and cæsium salts from carnallite by such operations as would not interfere with the usual process of working this mineral for its salts. This process may be briefly described as follows:—The coarsely-ground carnallite is dissolved in hot liquor, which has been obtained at a later stage in the working of a previous batch (see below), and the solution is poured off the residue into crystallising vats. The crystals are commercial potassium chloride; they are washed with cold water, and the washings (*decklaugen*) serve for dissolving a fresh batch of carnallite. The mother liquor from the potassium chloride crystals is evaporated, whereby sodium chloride (*bühnensalz*) is separated, and run into crystallising vats, where "artificial carnallite" crystallises; this is worked up again. The second mother liquor (*endlauge*) is used for the production of magnesium chloride and bromine. It will be seen that the products are (1) residue, (2) potassium chloride, (3) *decklaugen*, (4) artificial carnallite, and (5) *endlauge*. It was found that, notwithstanding the great solubility of rubidium and cæsium salts, the *endlauge* contains but little of them, and that they are distributed through the last four of the above mentioned products. Their presence in the artificial carnallite is to be explained similarly to the presence of potassium chloride in this product, which is due to the fact that, so long as the liquor contains less than 300 grams of magnesium chloride per litre, nearly pure potassium chloride crystallises; after this concentration has been reached, however, the double chloride of potassium and magnesium separates. Their presence in the commercial potassium chloride can be explained by the fact that, although a dilute solution of magnesium chloride at 20° can dissolve much more rubidium or cæsium chloride than of potassium chloride, the quantity of the former chlorides, soluble in stronger solution of the magnesium salt, falls off much more rapidly than is the case with potassium chloride, until it is found that in strong solutions of magnesium chloride the potassium salt is the more soluble. Thus, a solution of magnesium chloride, containing 50 grams per litre, dissolved 245 grams per litre of potassium chloride and 625 grams per litre of rubidium chloride; one containing 250 grams per litre dissolved 73 grams of potassium chloride and 168 grams of rubidium chloride; whilst one containing 400 grams of magnesium chloride dissolved 30 grams of potassium chloride and 6 grams of rubidium chloride. These observations are in accordance with the known fact that the double salts of rubidium and cæsium are less soluble than those of potassium; they also indicate that the *endlauge*, which contains some 360 grams of magnesium chloride per litre, should retain some 15 grams of rubidium chloride. This is certainly not the case; but the same applies to potassium chloride, which should be present to the extent of 34 grams per litre, whereas only 10 grams are found. The presence of magnesium sulphate and sodium chloride in the *endlauge* must be held to modify the conditions, even less of the chlorides in question being then soluble.

The existence of *rubidium carnallite*, $RbCl,MgCl_2,6H_2O$, being thus

indicated, the authors prepared the salt. It differs from potassium carnallite in that it crystallises unchanged from water, and is not decomposed by a small quantity of water. As might be expected, by analogy with the insolubility of rubidium and cæsium alums in a saturated solution of potassium alum, rubidium and cæsium carnallites proved much less soluble in magnesium chloride solution when potassium chloride was present. Thus, a solution containing 330 grams of magnesium chloride and 31 grams of potassium chloride per litre only dissolved 1·5 grams of rubidium chloride per litre (compare above).

It will be apparent, from what has been written, that the artificial carnallite must be regarded as containing the bulk of the rubidium and cæsium chlorides. By an elaborate series of crystallisations, based on the above observations, the authors succeeded in obtaining a carnallite rich in rubidium chloride; this was decomposed by hot sodium carbonate, the heat being continued until all ammonia (which also concentrates itself in the artificial carnallite) was expelled. By further recrystallisations from the filtrate, a potassium chloride, rich in rubidium chloride, was obtained; estimations of the rubidium in this, by the platinic chloride method, indicated that the original artificial carnallite contained 0·025—0·030 per cent. of rubidium chloride. A much better result was obtained by dissolving artificial carnallite in hot water, and adding more of the salt, until the liquor above the separated salts had reached the sp. gr. 33° B. The crystals then consisted of potassium chloride and carnallite, and showed, by analysis, the presence of 1·5 per cent. of rubidium chloride. From 12,000 kilos. of artificial carnallite, 1200 kilos. of this mixture were obtained. 1000 kilos. of this were further concentrated as follows:—Some of the salt was dissolved to saturation in hot water and crystallised; the mother liquor was boiled, again saturated with the salts, and again crystallised. More salts were dissolved in this second mother liquor, until its sp. gr. was 30° B., sodium chloride being thus separated; it was then evaporated to 31° B., whereby more sodium chloride and potassium chloride were eliminated. The clear liquor was finally crystallised, and 110 kilos. of a mixture of salts, containing 9·5 per cent. of rubidium chloride, were obtained. No crystallisation method will serve to enrich this product, because the isomorphism of potassium and rubidium salts causes them to crystallise in varying proportions at the concentration of such a mixture. To obtain pure rubidium chloride, a saturated solution of the 9·5 per cent. salt was precipitated, with constant stirring, by stannic chloride. (The presence of concentrated hydrochloric acid, as usually advised, was found to be unnecessary in the presence of so much magnesium chloride. The authors applied this method with success for concentrating the rubidium chloride prior to estimating it with platinic chloride.) The rubidium stannichloride was dissolved in a little water and reprecipitated by the addition of an equal volume of strong hydrochloric acid, this process being repeated six or seven times, until the line $K\alpha$ disappeared from the spectrum. The double chloride was then heated gently (to avoid the formation of stannates) with the calculated quantity of sodium carbonate, to convert the tin into stannic oxide.

The solution of the ignited mass contained chlorides of rubidium, cæsium, and sodium, and from it the rubidium was precipitated by sodium hydrogen tartrate; after several recrystallisations, pure rubidium hydrogen tartrate was obtained. The cæsium was separated from the concentrated mother liquors by stannic chloride; the double chloride was purified by several reprecipitations by concentrated hydrochloric acid, and decomposed by hydrogen sulphide; the cæsium chloride was finally precipitated with antimony trichloride, whereby, after two crystallisations from dilute hydrochloric acid, the pure salt $SbCl_3,6CsCl$ was obtained (Abstr., 1874, 816).

The isolation of the rubidium and cæsium can also be effected by dissolving 1 kilo. of the 9·5 per cent. salt in 2·5 litres of hot water, filtering, and adding a solution of 800 grams of aluminium sulphate in 800 c.c. of water. On cooling to 20°, rubidium and potassium alums crystallise; these can be separated by dissolving the mixture in $1\frac{1}{2}$ times its weight of hot water, and cooling to 40°. This is repeated until the lines Kα and Rbγ are about equally strong in the spectrum. An equal weight of water is then used, and the cooling carried to 35°. In all, seven to eight recrystallisations are necessary. The cæsium alum remains with the rubidium alum, and is separated by fractional crystallisation of the mixture from a little water at 60°; the cæsium alum crystallises in the first fraction, and is purified by recrystallisation from 20 times its weight of water. Precipitation with antimony trichloride may also be used. The conversion of the alums into other salts may be effected by well-known methods.

A. G. B.

Redetermination of the Atomic Weight of Cadmium. By H. N. Morse and H. C. Jones (*Amer. Chem. J.*, **14**, 261—273).—The authors have employed the method of converting the metal into nitrate, and, subsequently, into oxide, as used in the case of zinc (Morse and Burton, Abstr., 1888, 1247), and in the case of magnesium (Burton and Vorce, Abstr., 1890, 850). Cadmium, in the form of powder, was heated for a long time in hydrogen which had been purified by washing with acid and alkaline solutions of potassium permanganate, and then distilled, as in the preparation of pure zinc. The sixth distillate was examined spectroscopically by Rowland, and found to be free from all impurities which can be thus detected. This product was dissolved in nitric acid (purified as in the zinc determination), and, subsequently, treated in the same manner as with zinc, the porcelain crucible employed being always weighed against a second tared crucible, subjected to the same treatment as itself.

As cadmium oxide attacks porcelain vigorously at the temperature of the muffle-furnace, the final heating was carried out in a bath consisting of a nickel crucible, heated for two or three hours over the blast-lamp. Any possible contact of the oxide with the reducing gases of the flame was avoided by forcing the nickel crucible tightly into a hole in an asbestos board. The completeness of the decomposition was ascertained by testing the oxide with pure potassium iodide and hydrochloric acid.

Ten successive determinations gave results varying between 112·053 and 112·086 (O = 16), mean 112·0705, from total oxide and

total cadmium, 112·0706. This result agrees best with those of Von Hauer (mean of 9, 111·940) and Lenssen (mean of 3, 112·067), but differs considerably from Partridge's results (Abstr., 1891, 390 and 399); hence the authors have also carried out a series of determinations by the conversion of the oxalate into oxide, to compare with those Partridge obtained by that method. The mean of five determinations (varying from 111·981 to 112·051) made in this way was 112·025, as compared with the number 111·809 obtained by Partridge, and 112·036 by Lenssen (O = 16 and C = 12·001).

The number 112·0706 is regarded as more accurate than the number 112·025, as, in the oxalate method, the atomic weight of carbon is involved, the oxalate is strongly hygroscopic, and there is danger of loss by reduction to, and volatilisation of, metal.

W. T.

Crystals of Metallic Cadmium. By G. H. Williams (*Amer. Chem. J.*, **14**, 273—276).—Cadmium is hexagonal and holohedral, and thus, along with zinc and magnesium, confirms the suggestion of Brögger and Flinck, derived from the analogy of these metals with beryllium (*Zeit. f. Kryst.*, **9**, 1884, 236).

The cadmium crystals were produced by distillation in a vacuum. Polyhedral aggregates were abundant and large, but crystals suitable for measurement were very small. The largest individuals were barrel-shaped, like those of zinc, and resembled piles of basal plates; their side planes were often uneven and bent. The most minute crystals show pyramidal faces of comparative perfection, which, however, yield compound reflections.

Cadmium crystals show only the three faces 0P, P, and ∞P, and have a tendency to hemimorphic development. The axial ratio is $a : c :: 1 : 1{\cdot}6554$.

A comparison between the axial ratios of the four rhombohedral and four holohedral hexagonal elements throws zinc into the rhombohedral division with bismuth, antimony, tellurium, and arsenic, rather than with beryllium, magnesium, and cadmium. Zinc crystals occasionally show a rhombohedral alternation of the faces of certain pyramids, but otherwise appear to be holohedral. W. T.

Mercury Phosphide. By Granger (*Compt. rend.*, **115**, 229—230).—Mercury and phosphorus are without action on one another, even when heated together in sealed tubes. If, however, mercury and phosphorus iodide are heated together in sealed tubes at 275—300° for 10 hours, mercuric iodide and phosphide are obtained. The iodide is removed by treatment with potassium iodide solution, and the phosphide is left in brilliant crystals with a metallic lustre. They have the composition Hg_3P_2, and belong to the hexagonal system, showing the faces p and a', combined with a hexagonal prism. The crystals are red by transmitted light and yield a brown powder.

Mercuric phosphide is stable at the ordinary temperature, but splits up into phosphorus and mercury when heated. When heated in air, it burns, and when finely powdered and mixed with potassium chlorate, it detonates under the hammer. If thrown into chlorine, it burns

at the ordinary temperature. Nitric and hydrochloric acids are without action separately, but aqua regia dissolves it readily.

Mercury phosphide can also be obtained by passing phosphorus iodide over mercury heated at about 250°, but the separation of the two products is then difficult and tedious. C. H. B.

Mineralising Influence of Ammonium Sulphate. By T. Klobb (*Compt. rend.*, **115**, 230—232).—When lead sulphate is heated with excess of ammonium sulphate until the whole of the latter is just volatilised, a greyish, microcrystalline powder is obtained, consisting of short, transparent prisms resembling those of anglesite; sp. gr. = 6·28. They have the composition of normal lead sulphate.

As a rule, the ammonium sulphate seems to form intermediate double salts. With copper sulphate, this is especially distinct, and the products obtained at different temperatures are (1) $2CuSO_4,(NH_4)_2SO_4$; (2) $CuSO_4$; (3) $2CuO,SO_3$; (4) CuO. The first forms pale green prisms; sp. gr. about 2·85. It is very soluble in water, and when exposed to air rapidly becomes blue and opaque, 42 per cent. of water being absorbed at 20° in 42 days. The second forms distinct prismatic crystals of sp. gr. 3·78; they are less hygroscopic than the double salt, but gradually absorb water when exposed to the air. The basic sulphate is opaque and brownish-yellow, but retains the form of the normal sulphate; sp. gr. = 4·21. The oxide obtained by strongly heating the basic sulphate is crystalline and non-hygroscopic; sp. gr. = 6·36. C. H. B.

Micrographic Analyses of Alloys. By G. Guillemin (*Compt. rend.*, **115**, 232—234).—When the polished surface of an alloy is treated with dilute cold nitric acid, or with sulphuric acid of 10 per cent., under the influence of a feeble electric current (2 volts and 1 ampère), and the corroded surface is examined under a microscope, figures are obtained which vary with different alloys, but are invariably the same for the same alloy. These images can be photographed; they consist of more or less tortuous furrows, separated by ridges of unattacked metal. There seems little doubt that the alloys at the moment of solidification undergo partial liquation, and separate into several simple alloys of definite composition.

The examination of these surfaces makes it possible to classify ordinary alloys into a limited number of groups. In the case of bronze and brass, for example, it is possible to distinguish bronzes with a tin base, phosphor bronzes, brass containing less than 37 per cent. of zinc, Muntz metal, and brass containing more than 37 per cent. of zinc, aluminium bronze, aluminium brass, Delta metal, Roman bronze, &c. In white alloys, the presence of lead can be recognised, and its quantity estimated with close approximation. Ingots of copper from the same melting, but different stages of casting, show clearly the different degrees of refining. The presence of very small quantities of aluminium or phosphorus in brass or bronze can be detected with certainty. The presence of 4 per cent. or more of zinc in a tin bronze seems to mask the micrographic character of the phosphorus.

With one and the same alloy, the figures indicate differences in the mode of casting and cooling, and in mechanical treatment.

C. H. B.

Earths of the Cerium and Yttrium Groups. By A. Bettendorff (*Annalen*, **270**, 376—383).—In a previous paper (Abstr., 1891, 984), the author described the separation of the samarium earths from those of terbium and gadolinium; he has now investigated the solution containing the yellowish-red earth, RO = 119·96.

When the concentrated solution of the nitrates of the terbium and gadolinium earths is fractionally precipitated with ammonia, and the operation repeated systematically, there is finally obtained a dark brown earth, RO = 122, which consists for the most part of terbium earth; the relatively more basic oxide, RO = 119·68, has only a slight yellow tinge, and consists principally of the gadolinium earth. A spectroscopic examination of the concentrated solutions of the nitrates of these two oxides showed that the whole of the samarium originally present in the mixture, RO = 119·96, had accumulated in the gadolinium earth, the terbium earth being quite free from samarium. For the further purification of the gadolinium earth, it is submitted to systematic fractional precipitation with dilute ammonia; the samarium which accumulates in the first fractions is then removed by precipitating a concentrated solution of the nitrates with potassium sulphate, in the manner already described (*loc. cit.*). The first fractions of the gadolinium earth, purified in this way, were found to have an equivalent RO = 119·9; the last fractions were found to have an equivalent RO = 120·09—120·16, and gave on spectroscopic examination only indications of the absorption lines of the samarium earths, the indications being somewhat more decided in the first fractions. The combined fractions were, therefore, converted into the nitrate, the solution treated with a saturated solution of potassium sulphate, and the mixture kept for three days, with frequent shaking; the precipitated double salt and the excess of potassium sulphate were then separated. The double salt obtained after the third such treatment contains an earth, RO = 119·83, which, as a nitrate, shows only very feebly the absorption lines of samarium. The gadolinium earth in solution has the equivalent RO = 120·18 or R_2O_3 = 360·54, so that its atomic weight is R = 104·22 or R‴ 156·33, as the average of three determinations; a spectroscopic examination of a concentrated solution of its nitrate showed only faint indications of the presence of samarium, and the absence of all other absorption lines.

The strongly ignited gadolinium earth is of a faint yellow colour, and dissolves freely in acids, yielding colourless salts; when gently heated in a stream of hydrogen, it becomes colourless, but without change in weight; on strongly igniting the oxide in an atmosphere of hydrogen, it loses weight (0·11 per cent.) and seems to undergo partial reduction, assuming a faint, greyish hue; on heating in the air, it regains its original weight and its original colour; when the greyish oxide is treated with very dilute hydrochloric acid in the cold, there remains a small quantity of a substance of a rather darker shade. The spectrum of the gadolinium earth shows an orange-red line of great brightness and sharpness, the centre of which has the wave-

length $\lambda = \mu\mu$ 6094; there are also to be seen indications of bands, but they are extremely feeble. The author could not obtain the spark spectrum of gadolinium chloride which has been described by Lecoq de Boisbaudran (*Compt. rend.*, **111**, 472). F. S. K.

Action of Superheated Water and Solutions of Alkalis and of Salts on Glass. By F. Foerster (*Ber.*, **25**, 2494—2518; compare Abstr., 1889, 828; Weber and Sauer, this vol., p. 1052).—When a sealed glass tube, partially filled with water, is heated in aniline vapour for six hours, the portion exposed to the action of the vapour alone, becomes coated with a white, opaque layer, consisting chiefly of alkali silicates, together with calcium silicate and a small quantity of aluminium silicate. The superheated water acts in the same manner as at a lower temperature. Experiments made with different kinds of boiler-gauge glass showed great variation in their stability to superheated water; the glass specially prepared at Jena for this purpose giving the best results.

Solutions of caustic alkalis have a much stronger action on glass than water, inasmuch as they dissolve the glass as a whole, and not merely certain portions of it. Of equivalent solutions of the alkalis, soda has the strongest action, then potash, ammonia, and baryta in the order given; in all cases the action is greater the higher the temperature. At the ordinary temperature, dilute solutions act on the glass more readily than concentrated, but at higher temperatures the action increases with increase of strength, first very rapidly and then more slowly; pure solutions of the alkalis act much less readily than those containing small quantities of silicic acid as impurity. The extent of the action in all these cases is, as would be expected, dependent on the nature of the glass.

Solutions of the alkali carbonates attack glass more rapidly than water, but the nature of their action corresponds more with that of salts than with that of the alkalis. The action of other salts appears to depend partly on the concentration and nature of the salt, and partly on the reactions which take place between it and the substances extracted from the glass. H. G. C.

Analysis of Slag of Metallic Appearance from the Manufacture of Phosphorus in Electrical Furnaces. By J. C. Chorley (*Chem. News*, **65**, 301—302).—In the manufacture of phosphorus from a mixture of natural aluminium phosphate, calcium phosphate, carbon, and sand in an electrical furnace, two kinds of slag are obtained: the predominating one consists chiefly of calcium and aluminium silicates; the other, apparently a mixture of iron silicides and phosphide in varying proportions, yielded in the analysis of three samples from about 68 to 74 per cent. of iron, 9 to 14 per cent. of phosphorus, and 10 to 19 per cent. of silicon. It is found distributed through the mass in very hard, brittle buttons, of a steel-grey colour, and appears quite homogeneous, but not crystalline. Its sp. gr. is 5·965, its sp. heat 0·146, and it conducts electricity. It is not attacked by hydrofluoric, hydrochloric, nitric, nitrohydrochloric, or dilute sulphuric acid, and is only partially decomposed when boiled

with concentrated sulphuric acid; it is, moreover, only superficially affected by hydrogen sulphide, and but slightly acted on by bromine or iodine. To decompose it for analysis, it is either heated, in a finely-powdered condition, in a current of chlorine, when the iron, phosphorus, and silicon volatilise as chlorides, silica alone remaining behind; or it is heated with excess of a neutral solution of copper sulphate in a closed tube, at 170°, for 4 or 5 hours; no gas is evolved, plenty of copper mixed with copper phosphide is precipitated, and some iron, phosphorus, and silicon are dissolved. The contents of the tube are treated with nitric acid and the undissolved residue is fused with fusion mixture before examination in the ordinary way; whilst the nitric acid solution is evaporated with hydrochloric acid, the silica estimated, the copper removed as sulphide, and the solution containing some of the iron, &c., mixed with the main solution at the proper stage. D. A. L.

The Action of Nitric Acid on Metals. By C. Montemartini (*Gazzetta*, **22**, 384—397, 397—407, 426—436; compare this vol., p. 1278).—Much contradiction exists as to the changes which occur when nitric acid acts on tin. The author finds that the acid, up to a concentration of 12 per cent., always attacks tin with formation of stannous salt, which partially decomposes, forming a turbid solution; gas is always evolved, although slowly. Nitric acid from 12 to 45 per cent. completely dissolves the metal to a yellow solution, with abundant evolution of gas; the solution, when left, slowly becomes turbid, but the precipitation may be retarded by adding hydrochloric acid. The tin is present in these solutions as stannous nitrate, and the turbidity is due partly to the oxidation of this salt and partly to its conversion into insoluble stannous compounds, which, in turn, yield stannic hydrate. Nitric acid of more than 45 per cent. concentration does not dissolve tin, but converts it into a white substance. If 70 per cent. acid is used, this white oxidation product is soluble in water, but the solution, after a few seconds, becomes turbid, and stannic hydrate is deposited; the addition of hydrochloric acid to the clear solution greatly retards the precipitation. The soluble, white substance is found by analysis to be stannic nitrate, $Sn(NO_3)_4$; it is stable in presence of concentrated nitric acid at 90°, but is immediately decomposed at 100°.

The solution of 1 gram of tin in excess of 27·5 per cent. acid yields 0·0180 gram of ammonia, 0·1060 gram of nitrous oxide, and 0·0051 gram of nitrogen. The maximum quantity of ammonia is obtained when 1 per cent. nitric acid is used, but the rate of diminution in the amount of this gas produced, as stronger acid is used, is small; even 70 per cent. acid causes the formation of much ammonia. The hypothesis that the nitric acid is reduced by nascent hydrogen is insufficient for the explanation of the phenomena observed during the action of nitric acid on tin.

Contrary to the statements of Personne (*Bull. Soc. Chim.*, 1864, i, 163) and Maumené (*Ann. Chim. Phys.* [4], **3**, 343), the action on antimony of nitric acid, varying in concentration from 2 to 70·27 per cent., does not yield appreciable quantities of ammonia; 2 per cent.

acid has very little action on the metal. Antimony is not dissolved by nitric acid; a white powder always remains; when 70 per cent. acid is used, this residue seems to have the composition $(SbO)NO_3$. Nitric peroxide is practically the sole gas produced when this metal is used.

Molybdenum is attacked by 3 to 70 per cent. acid without the formation of ammonia. Concentrated acid (70 per cent.) attacks the metal but slowly; a much more vigorous action occurs with weaker acid (50 per cent.), and a reddish solution and residue are obtained. The solution reduces permanganate, so that the metal is not immediately converted into molybdic anhydride by 50 per cent. acid, but a nitrate would seem to be first formed; 70 per cent. acid at once gives molybdic anhydride. The quantity of nitric oxide produced in the reaction between nitric acid and molybdenum decreases as the concentration of the acid increases; nitric peroxide is the main gaseous product with 50 per cent. acid. Neither nitrogen nor nitrous oxide is formed.

No appreciable amount of ammonia is produced in the reaction between copper and 3 or 27·5 per cent. nitric acid. Dilute acid (below 30 per cent.) yields only nitric oxide and nitrous acid; with stronger acid, the gas evolved is principally nitrogen tetroxide, but small quantities of the trioxide are also formed. With acid of less than 30 per cent. concentration, the reaction is represented by the equation $Cu + 3HNO_3 = Cu(NO_3)_2 + HNO_2 + H_2O$. Nitric oxide is then formed in accordance with the equation $3HNO_2 = 2NO + HNO_3 + H_2O$. Nitric peroxide only is obtained with 70 per cent. acid.

Below 15°, nitric acid of all concentrations attacks pure lead very slowly; rather dilute acid acts the most rapidly. Small quantities of ammonia are formed, the amount being greatest with weak acid.

The action of nitric acid (27·5 and 70 per cent.) on bismuth yields neither ammonia, nitrogen, nor nitrous oxide. More nitric oxide is obtained with dilute than with concentrated acid, and owes its origin to secondary action. 27·5 per cent. acid gives no nitric peroxide, but this gas is the main product if 70 per cent. acid be employed.

The reaction between nitric acid and aluminium proceeds very slowly; with 27·5 per cent. acid no ammonia was obtained.

Mercury yields no ammonia with 27 and 50 per cent. acid; the quantity of nitric oxide produced, diminishes as the concentration increases. 27·5 per cent. acid gives no nitric peroxide, but stronger acid yields large quantities just as in the cases of copper and bismuth. Mercurous nitrate is obtained in solution on operating with 25 per cent. acid; more concentrated acid (50—70 per cent.) gives the mercuric salt.

Nitric acid (27·5 per cent.) gives no ammonia with silver, but only nitric oxide and nitrous acid.

The amount of ammonia produced in the reaction between magnesium and nitric acid increases with the concentration of the latter until 40 per cent. acid is reached, the quantity then decreases. Much hydrogen is formed; the mixture of this gas and nitric oxide liberated by 13 per cent. acid may be exploded by an electric spark.

Ammonia is produced by the action of nitric acid on manganese; so much hydrogen is formed that the evolved gas will not explode until oxygen has been added. Nitrogen and nitrous oxide are also liberated.

In all the previous experiments, excess of nitric acid was employed and the temperature was kept constant (15—20°).

The metals may be classed in three groups, according to their behaviour towards nitric acid. To the first group belong those metals which, with nitric acid, yield only nitrous acid, nitric oxide, nitrogen trioxide, and nitric peroxide. Metals of the second group give, besides these products, hyponitrous acid, nitrous oxide, nitrogen, and ammonia. In addition to these, metals of the third group liberate hydrogen. It is to be noted that metals belonging to the first group either do not decompose water at all or only at very high temperatures. Metals of the second group decompose water at much lower temperatures, and those of the third group act on water either at ordinary or at comparatively low temperatures. There is hence a relation between the products of the action of nitric acid on metals and the behaviour of the metals towards water; this relation supports the author's view that water sometimes takes part in the reaction.

The author considers that the reaction between nitric acid and metals which do not decompose water may be represented by the equation

$$M + 3HNO_3 = M(NO_3)_2 + HNO_2 + H_2O,$$
$$\text{or } M + 4HNO_3 = M(NO_3)_2 + 2NO_2 + 2H_2O,$$

according as the acid used is dilute or concentrated. To explain the formation of nitrogen trioxide, the following equation is employed, $2M + 6HNO_3 = 2M(NO_3)_2 + N_2O_3 + 3H_2O$. When water plays a part in the reaction, a more complex series of equations is necessary.

W. J. P.

Mineralogical Chemistry.

New Silver Ore. By H. N. Warren (*Chem. News*, **66**, **42**).—Hard, horny particles of ore containing traces of gold and silver iodide, bromide, and chloride, either, as in some samples, alone, as in others associated together, have been found disseminated through kaolinised deposits in the Broken Hill district of Australia.

D. A. L.

Jacobsite and Braunite from Sweden. By L. J. Igelström (*Zeit. Kryst. Min.*, **20**, 375; from *Geol. Fören. Förh.*, **12**, 137—139).—At the Glakärn mine, in the parish of Linde, the predominating ores are jacobsite and braunite. An analysis of the former mineral gave the following results:—

Fe_2O_3.	MnO.	MgO.	Insoluble in hydrochloric acid.
57·55	36·74	0·72	6·02

This is a new locality for these two minerals. B. H. B.

Braunite and Friedelite from Sweden. By G. Flink (*Zeit. Kryst. Min.*, **20**, 368—372; from *Bihang Sv. Vet. Akad. Handl.*, **16**, 1—23).—1. *Braunite from Långbanshyttan.*—The author has made a crystallographical examination of this mineral, and has observed five new planes: $4P\infty$, P2, $\frac{3}{4}P\infty$, $\frac{6}{5}P\frac{3}{2}$, and $\frac{5}{4}P\frac{5}{2}$. The planes ∞P and $P\infty$, observed by the author, have previously been noticed on braunite from other localities, but are new for braunite from Långbanshyttan. An analysis of this mineral gave the following results:—

SiO_2.	MnO.	O.	FeO.	CaO.	MgO.	Total.
9·89	78·91	7·35	3·81	0·34	0·15	100·45

This composition corresponds with a mixture of $MnMnO_3$ with $(Mn,Fe,Ca,Mg)SiO_3$. The sp. gr. of the mineral is 4·72.

2. *Friedelite from Harstigen.*—Although pyrosmalite hitherto has been found only in Sweden, the corresponding manganese mineral, friedelite, has been found only at Adervielle, in the Pyrenees. In 1889 it was, however, discovered at the Harstig mine in small crystals with pyroxene, magnetite, chlorite, and galena. The crystals are transparent and of a pink colour, with a hardness of 4 to 5, and a sp. gr. of 3·058. Analysis gave the following results:—

SiO_2.	Cl.	MnO.	FeO.	CaO.	MgO.	Mn.	H_2O.	Total.
34·66	4·04	42·48	4·08	0·53	2·27	3·13	8·47	99·66

B. H. B.

Limonite in Texas. By R. A. F. Penrose (*Jahrb. f. Min.*, 1892, ii, Ref. 18; from *First Annual Report Geol. Survey of Texas*, 66—83).—Limonite beds, 1 foot to 3 feet in thickness, overlying glauconite sands, occur in Cherokee, Anderson, and other counties in the east of Texas. The ore is sometimes laminated, sometimes massive or forming botryoïdal masses. The origin of the laminated and massive varieties is traced to the weathering of iron pyrites, and that of the botryoïdal masses to the oxidation of iron carbonate. The author gives numerous analyses, three of which are as follows:—

	Fe_2O_3.	Al_2O_3.	MnO.	MgO.	CaO.	SO_3.	SiO_2.
I.	59·20	11·20	—	—	trace	—	16·20
II.	65·79	8·31	—	trace	2·30	0·36	18·77
III.	74·11	16·50	0·13	1·77	1·04	0·93	1·49

	K_2O.	Na_2O.	P_2O_5.	Loss.	Total.
I.	—	—	trace	13·45	100·05
II.	—	—	trace	5·05	100·48
III.	0·36	0·49	0·12	—	97·94*

* In the original this total is given as 98·08.

I. Massive ore, Henderson Co. II. Laminated ore, north-east corner of Upshur Co. III. Limonite geode from Berry Hill, Marion Co. B. H. B.

Titaniferous Iron Ore and Manganese Spar from the Fichtelgebirge. By F. v. Sandberger (*Jahrb. f. Min.*, 1892, ii, Mem. 37—43).—1. *Titaniferous Iron Ore.*—The Eger contains at several places black metallic grains, undoubtedly produced from disintegrated lithionite-granite. A large quantity of this mineral from the sand at Röslau showed that the form of the grains is hexagonal with a tabular development. The colour is dark steel-grey, the streak black, and the sp. gr. 4·659. The ore is non-magnetic. Analysis gave the following results :—

TiO_2.	Fe_2O_3.	FeO.	MgO.	Total.
48·12	24·95	27·96	0·29	101·32

2. *Manganese-spar from Arzberg.*—At Arzberg a manganese carbonate has recently been discovered. It forms a thick layer on chalybite. Its sp. gr. is 3·59. Analysis yielded :—

$MnCO_3$.	$FeCO_3$.	$CaCO_3$.	SiO_2.	Total.
84·41	14·22	0·54	0·40	99·57

This is the richest in iron of all the manganese spars hitherto analysed.

The remainder of the author's paper is devoted to descriptions of (3) margarodite, a secondary mica from the lithionite-granite of Epprechtstein, (4) pseudomorphs of chlorite after orthoclase from the Strehlenberg, (5) pseudomorphs of quartz after orthoclase from the same locality, and (6) lithium-mica from Tröstau, near Wunsiedel, a mica very similar in composition to that from the pegmatite of Penig, in Saxony. B. H. B.

Triplite and Kaolin from the United States. By L. G. Eakins (*Zeit. Kryst. Min.*, **20**, 494; from *Bull. U.S. Geol. Surv.*, **60**, 135—136).—The specimen of triplite analysed (I) was obtained from a tin mine at Rapid City, South Dakota. It is of a brown colour, and translucent in small fragments. The kaolin analysed (II) forms a fine white mass, filling the cavity in the Rodwell Basin, Gunnison Co., Colorado. In it crystals of pyrites and galena are found. The analyses gave :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	K_2O.	Na_2O.	Li_2O.
I.	0·43	8·74	2·36	1·97	29·13	6·72	trace	5·25	0·13
II.	47·28	36·19	trace	—	—	0·42	5·74	0·51	—

	P_2O_5.	H_2O.	F.	Cl.	CO_2.	Total.
I.	39·68	3·67	2·35	0·25	0·26	100·94
II.	0·57	8·72	—	—	—	99·43

B. H. B.

Manganese-spar and Celestine from Scharfenberg. By H. Zinkeisen (*Jahrb. f. Min.*, 1892, ii, Ref. 68—69).—In a geological

description of the Güte Gottes mine at Scharfenberg, on the left bank of the Elbe above Meissen, the author gives analyses of the manganese-spar (I) characteristic of the deposit, and of celestine (II) which is of frequent occurrence in well developed crystals. The analytical results were as follows :—

	MnO.	SrO.	FeO.	CaO.	MgO.	BaO.	CO_2.	SO_3.	Total.
I.	52·40	trace	5·13	3·06	0·77	trace	38·53	—	99·89
II.	—	55·32	—	0·80	—	0·18	—	44·10	100·40

B. H. B.

Minerals from the Pacific Coast. By W. H. Melville and W. Lindgren (*Zeit. Kryst. Min.*, **20**, 495—498; from *Bull. U.S. Geol. Surv.*, **61**, 11—31).—1. *Sulphates.*—The author gives analyses of three sulphates found in strings in a black opal at the Redington Quicksilver mine, Knoxville, California. The first occurs in small, black, regular crystals, and is a double sulphate of potassium and iron. The second consists of fibrous masses of redingtonite (sp. gr. 1·761), and the last, termed *knoxvillite* by the authors, forms thin crusts on the redingtonite. Analyses are also given of copiapite from the same locality, and of a yellow sulphate from the Sulphur Bank, Lake Co., California, which was found optically to be identical with copiapite. As all these salts were moist, the proportion of water cannot be utilised in the discussion of their formulæ; the molecular ratios of the anhydrous salts were :—

Redingtonite	$6RO,4R_2O_3,19SO_3$,
Knoxvillite	$6RO,6R_2O_3,15SO_3$,
Copiapite	$3RO,6R_2O_3,17SO_3$,
Yellow sulphate (Sulphur Bank)	$3RO,9R_2O_3,25SO_3$.

2. *Stromeyerite.*—An analysis is given of stromeyerite from the Silver King mine, Calico, San Bernardino Co., California. The ore is of a dark, steel-grey colour, and is accompanied by barytes, malachite, and a brown manganic oxide. Its sp. gr. is 6·28. The analytical results were :—

Ag.	Cu.	S.	Fe.	Residue.	Total.
53·96	28·57	15·51	0·26	1·55	99·85

The residue consists of barytes with a little quartz. B. H. B.

Thaumasite, Wollastonite, Chabasite, and Vesuvian. By O. Widman (*Zeit. Kryst. Min.*, **20**, 373—375; from *Geol. Fören. Förh.*, **12**, 20—29).—1. *Thaumasite.*—This mineral has been found between apophyllite in veins in gneiss at Kjölland, 13 miles from the best known locality for this mineral, the Bjelkes mine, at Åreskutan. Analyses of the mineral from the two localities gave results corresponding with the formula $CaSiO_3,CaCO_3,CaSO_4,15H_2O$.

2. *Wollastonite from Perheniemi, Finland.*—Two varieties were analysed, one with a vitreous lustre and laminated texture, the other with a silky lustre and fibrous texture. The results were as follows :—

SiO_2.	CaO.	FeO.	H_2O.	Total.
51·49	47·65	0·26	0·60	100·00
51·23	47·37	1·08	0·32	100·00

3. *Chabasite from the Faroe Islands.*—The mean of three analyses of this mineral was as follows:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
45·85	19·83	8·86	2·35	0·63	22·26	99·78	2·09

The formula is therefore $Ca(Na_2K_2)SiO_3,Al_2(SiO_3)_3,6H_2O$.

4. *Vesuvian.*—The author gives the following results of analyses of vesuvian (I) from Arendal and (II) from Hamrefjeld, Norway:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	B_2O_3.
I.	35·45	—	12·18	7·29	1·88	34·01	4·56	1·96
II.	35·19	1·63	11·53	5·74	2·00	38·34	2·72	—

	F.	H_2O.	Total.	
I.	—	3·14	100·47	
II.	1·97	0·89	100·01	B. H. B.

Pholidolite, a New Mineral. By G. Nordenskiöld (*Zeit. Kryst. Min.*, **20**, 382—386; from *Geol. Fören. Förh.*, **12**, 348—358).—In cavities in the Taberg mine in Wermland, Sweden, fine crystals of diopside, garnet, and other minerals occur, together with an earthy mass which fills the cavities. This mass consists of yellow scales with crystals of diopside, garnet, epidote, apatite, titanite, magnetite, chlorite, and galena. It is, in fact, a kind of crystal-breccia. The yellow scales appear to belong to a new mineral, for which the author suggests the name of *pholidolite*. The sp. gr. of the mineral is 2·408. The analysis of the mineral gave results corresponding with the formula $13SiO_2,Al_2O_3,12(FeMg)O,K_2O,5H_2O$, and the author considers that the mineral is composed of the following compounds:—

1 magnesium silicate	$Mg_6Si_3O_{12},H_4Si_5O_{12}$.
$\frac{1}{3}$ potassium mica silicate	$K_2Al_2Si_2O_8$.
1 silicate	$H_3Mg_3(MgOH)_3Si_3O_{12}$.

B. H. B.

The Pyroxene Family. By E. A. Wülfing (*Jahrb. f. Min.*, 1892, ii, Ref. 23).—The author has endeavoured to determine the relations between the chemical composition and the optical properties of augites, especially of those free from alumina. The pyroxenes examined were: 1. Diopside from Nordmarken, type V. 2. From the Alathal. 3. From Nordmarken, type IV. 4. From Nordmarken, type I. 5. Hedenbergite from Tunaberg. 6. Ægirine from Langesundfjord. With regard to the chemical composition of the diopsides, the author finds that they should be regarded neither as mixtures of $CaMgSi_2O_6$ with $CaFeSi_2O_6$, nor as mixtures of $CaOSiO_2$, $MgOSiO_2$, and $FeOSiO_2$, but as a mixture of three primary constituents, $CaOMgO2SiO_2$, $CaOFeO2SiO_2$, and $MgOFeO2SiO_2$. The percentage

amounts of the primary constituents are shown in the following table:—

	I.	II.	III.
$CaO,MgO,2SiO_2$	90·4	35·0	8·0
$CaO,FeO,2SiO_2$	8·6	60·4	84·8
$MgO,FeO,2SiO_2$	1·0	0·6	5·2
MgO,Al_2O_3,SiO_2.....	—	—	2·0
H_2O,SiO_2	—	1·4	—
Fe_2O_3,SiO_2	—	2·6	—
	100·0	100·0	100·0

I, mean of the composition of the first three diopsides; II, diopside of Nordmarken, type I; and III, hedenbergite. B. H. B.

Analyses of Pyroxene. By T. M. Chatard (*Zeit. Kryst. Min.*, **20**, 501; from *Amer. Geologist*, **6**, 35).—In a description of the non-felspathic intrusive rocks of Maryland, the author notes that the fine pyroxenite of Hebbville, west of Baltimore, consists of typical, reddish-brown bronzite (Analysis I) and of emerald-green diopside (Analysis II):—

	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	54·53	—	1·93	0·30	1·70	8·92	0·28	2·25
II.	51·80	0·13	2·21	0·51	1·29	3·50	trace	20·99

	MgO.	H_2O.	Total.	Sp. gr.
I.	29·51	1·14	100·56	3·300
II.	17·76	0·65	98·84	3·308

B. H. B.

Garnierite from Norway. By C. A. Münster (*Zeit. Kryst. Min.*, **20**, 402; from *Archiv. matematik naturvidenskab.*, **14**, 240).—At Foldalen, in Norway, this mineral occurs in a thin layer. On analysis, it gave the following results:—

SiO_2.	MgO.	NiO.	FeO.	H_2O.	Total.
44·55	21·03	5·45	9·87	18·71	99·61

The surrounding rock contains 0·33 per cent. of nickel.

B. H. B.

Allanite from Gyttorp, Sweden. By G. Nordenström (*Zeit. Kryst. Min.*, **20**, 386—387; from *Geol. Fören. Förh.*, **12**, 540).—In a recently-opened iron mine at Gyttorp, allanite has been discovered in great abundance. It occurs in granulite as lenticular masses surrounded by dark mica. Analysis of the mineral gave the following results:—

SiO_2.	$Fe_2O_3 + Al_2O_3$.	FeO.	Ce_2O_3.	CaO.	MgO.	H_2O.	Alkalis and loss.
29·60	21·42	9·51	24·72	7·75	4·25	0·67	2·18

B. H. B.

Gadolinite. By C. W. Blomstrand (*Zeit. Kryst. Min.*, **20**, 366).—Analyses of gadolinite from Ytterby (I) and from Hitterö (II) gave results in good accord with the formula $Be_2Fe(YO)_2(SiO_4)_2$, which the author regards as the rational formula for gadolinite. The analytical results were as follows:—

	SiO_2.	ThO_2.	Ce_2O_3.	$(La,Di)_2O_3$.	$(Y,E)_2O_3$.	Al_2O_3.	Fe_2O_3.	FeO.
I.	23·84	0·31	0·92	3·33	47·06	0·12	0·21	12·97
II.	23·72	0·35	6·67		45·62	—	—	12·19

	MnO.	BeO.	MgO.	CaO.	PbO.	Na_2O.	Total.
I.	0·12	10·55	0·07	0·35	0·05	0·18	100·08
II.	0·16	10·10	0·26	0·37	0·05	0·19	99·68

B. H. B.

Gadolinite. By W. Petersson (*Zeit. Kryst. Min.*, **20**, 376—383; from *Geol. Fören. Förh.*, **12**, 275—347).—The author has made an exhaustive study of the composition of gadolinite, and his paper contains the results of analyses of this mineral from Hitterö, from Ytterby, from Broddbo, from Finbo, from Gamla Kårarfvet, from Nya Kårarfvet, from Torsåker, from Karlberg, from Grimstad, and from other Scandinavian localities. The investigation has led to the conclusion that gadolinite is characterised by a constant fairly high proportion of beryllium, regardless of the locality from which the mineral is derived and of its physical condition. The view hitherto held that gadolinite existed free from beryllium or poor in that metal has thus not been confirmed. The author therefore adopts for gadolinite the formula $Be_2FeY_2Si_2O_{10}$ or $Be_2Fe(YO)_2(SiO_4)_2$ (compare Abstr., 1891, 1168). B. H. B.

The Formula of Tourmaline. By A. Kenngott (*Jahrb. f. Min.*, 1892, ii, Mem. 44—57).—This paper was suggested by the publication of three analyses by R. Scharizer (Abstr., 1889, 764) of the tourmaline from Schüttenhöfen, in Bohemia. By calculations based on these three analyses and on 20 analyses of American tourmalines published by R. B. Riggs (Abstr., 1888, 659), the author concludes that the tourmalines form a series of silicates in which, if the oxides Al_2O_3, B_2O_3, Fe_2O_3, and Mn_2O_3 are grouped together as R_2O_3, the MgO, CaO, FeO, and MnO as RO, and H_2O, Na_2O, K_2O, and Li_2O as R_2O, two isomorphous silicates, A and B, are contained in varying quantities. For the silicate A the calculated formula is $3R_2O,SiO_2 + 5(R_2O_3,SiO_2)$, and for the silicate B the formula is $2(3RO,SiO_2) + R_2O_3,SiO_2$. The author's calculations were extended to the analyses of P. Jannasch and G. Calb (Abstr., 1889, 472; 1891, 24) and to those of Rammelsberg (Abstr., 1891, 24), so that altogether 45 analyses were considered. B. H. B.

Composition of Melilite. By J. H. L. Vogt (*Jahrb. f. Min.*, 1892, ii, Mem. 73—75).—The author points out that the composition of the artificial melilite formed during the burning of Portland cement in an annular kiln, and analysed by G. Bodländer (this vol.,

p. 416), does not accord with the theoretical composition of a mixture of gehlenite and akermanite, the two terminal members of which the melilite series, according to the author, is composed. Nor does the analysis agree with older analyses of natural melilite, Bödländer's analysis showing too much RO (CaO,MgO,K_2O,Na_2O). By a microscopical examination of some of Bödländer's original material, the author finds that, owing probably to the presence of cement-dust, the mineral was not chemically pure. For this reason, the analysis is not available either to confirm or to confute the author's theory of the composition of the melilite series. B. H. B.

Petalite, Spessartine, and Willemite. By F. W. Clarke (*Zeit. Kryst. Min.*, **20**, 493; from *Bull. U.S. Geol. Surv.*, **60**, 129).—Analyses of petalite from Peru, Maine, (I) forming white masses with pearly lustre, and of spessartine (II) from Amelia Co., Virginia, gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	Li_2O.	Na_2O.	Loss on ignition.
I.	77·29	19·95	trace	—	trace	—	2·62	2·39	1·03
II.	35·35	20·41	2·75	1·75	38·70	0·94	—	—	0·27

An analysis of willemite from the Trotto mine, Franklin, New Jersey, gave—

SiO_2.	ZnO.	Loss on ignition.
27·41	68·86	0·25

B. H. B.

Minerals of the Harstigen Mine, Sweden. By A. Hamberg (*Zeit. Kryst. Min.*, **20**, 387—402; from *Geol. Fören. Förh.*, **12**, 567—632).—1. *Manganophyll.*—The highly manganiferous mica from the Harstigen mine, near Pajsberg, in Wermland, was first observed by Igelström, and named manganophyll. Analysis of two varieties—I, reddish-brown, and II, dark-brown—gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	MnO.	FeO.	CaO.	MgO.	K_2O.
I.	40·64	9·43	3·66	—	9·63	0·05	—	22·31	10·50
II.	36·42	12·64	3·80	0·70	17·13	—	0·20	14·73	8·78

	Na_2O.	Li_2O.	H_2O.	F.	Total.
I.	0·35	0·29	4·30	0·30	101·46
II.	0·38	0·40	4·60	0·33	100·11

Although the composition of manganophyll does not accord with the formulæ for biotite proposed by Tschermak, Knop, Clarke, and others, there can be no doubt that this mineral should be regarded as a manganiferous biotite.

2. *Manganiferous Chlorite.*—This mineral occurs with manganophyll in veins filled with calcite. On analysis, it gave results corresponding with the formula

$$3(2H_2O,3MgO,2SiO_2) + 2(2H_2O,2MgO,Al_2O_3,SiO_2),$$

proposed by Tschermak for pennine, some of the magnesia being replaced by manganese.

3. *Ganophyllite.*—This new mineral, named after the high lustre (γάνος) of the laminæ (φύλλον) occurs in fairly large, monosymmetric crystals. Analysis gave results in accord with the formula

$$8SiO_2,Al_2O_3,7MnO,6H_2O.$$

4. *Pyrophanite.*—With ganophyllite, a second new mineral has been discovered. It is of a red colour, and proves to be a compound isomorphous with titaniferous iron ore, and having the composition $MnTiO_3$, analysis having given the following results:—

SiO_2.	TiO_2.	MnO.	Fe_2O_3.	Sb_2O_3.	Total.
1·58	50·49	46·92	1·16	0·48	100·63

This is the first titaniferous mineral found in Wermland.

B. H. B.

Helvine from Hungary. By A. Kalecsinszky (*Zeit. Kryst. Min.*, **20**, 365).—Helvine from Kapnikbánya, sp. gr. 3·203, gave on analysis the following results:—

SiO_2.	MnO.	BeO.	Mn.	FeO.	S.	Total.
32·82	36·40	13·45	9·02	0·66	5·25	97·60

B. H. B.

Products of the Weathering of Diabase. By R. Brauns (*Jahrb. f. Min.*, 1892, ii, Mem. 1—24).—Opposite Friedensdorf, near Marburg, on the left side of the Lahn, a diabase has been opened up by an extensive quarry. This diabase is of special interest on account of the numerous minerals of secondary formation occurring in fissures in it. It is for the most part a normal felspar-diabase, in which the augite can be detected with the naked eye, whilst the felspar is less distinct. The mass of rock has a columnar structure, and is traversed by numerous fissures, whose walls are covered with minerals of secondary formation, in some cases with analcime alone, with prehnite alone, with albite alone, or more frequently with prehnite, analcime, and calcite, or more rarely with these minerals together with albite. Natrolite occurs, but only to a subordinate extent. These minerals are described in detail by the author, and analyses of each are given. The order in which the minerals have been formed is probably as follows:—Analcime, albite, prehnite, prehnite and calcite, analcime of second formation, calcite. In some cases, however, albite is also older than analcime. In conclusion, the author discusses the manner in which these compounds have been produced from the weathering of lime-soda-felspar. The formulæ of these compounds are as follows:—

Lime-soda felspar: $Na_2Al_2Si_6O_{16}$	$Na_2Al_2Si_6O_{16}$	Albite.
	$Na_2Al_2Si_4O_{12},2H_2O$ ..	Analcime.
	$Na_2Al_2Si_3O_{10},2H_2O$ ..	Natrolite.
$Ca_2Al_4Si_4O_{16}$	$H_2Ca_2Al_2Si_3O_{12}$	Prehnite.
	$HCa_2Al_3Si_3O_{13}$	Epidote.
	$CaCO_3$	Calcite.

B. H. B.

Analcime as a Rock-forming Mineral. By W. Lindgren (*Zeit. Kryst. Min.*, **20**, 498—499; from *Proc. Calif. Acad. Sci.*, **3**, 39).—In the Cretaceous sandstones of the Highwoods, Rocky Mountains, in Montana, veins occur of a basaltic rock composed of augite, olivine, magnetite, and crystals of analcime. An analysis of the crystals (sp. gr. 2·20) gave—

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
54·90	23·30	1·90	0·70	10·40	1·60	7·50	100·30

B. H. B.

Proportion of Fluorine in Fossil Bones of Various Ages. By A. Carnot (*Compt. rend.*, **115**, 243—246).—The proportion of fluorine in fossil bones is very much higher than in recent bones. In fossils from primary and secondary rocks, the ratio of fluorine to phosphoric acid is practically the same as in crystallised apatite. In tertiary and quaternary fossils, the proportion of fluorine is distinctly lower, and it gradually decreases with the age of the formation, always, however, remaining considerably higher than in recent bones. This fact may possibly be utilised to distinguish recent bones from quaternary bones with which they may have become mixed, but such a method would not be applicable to bones from different beds.

C. H. B.

New Meteorites. By E. E. Howell (*Jahrb. f. Min.*, 1892, ii, Ref. 33—36; from *Proc. Rochester Acad. of Science*, **1**, 86—100).—The author gives further particulars of the Welland, the Hamilton Co., the Puquois, the De Cewsville, and the El Chañaralino meteorites. He also describes two meteorites, the Doña Inez and Llano del Inca, found in Atacama, Chili, in 1888, during the survey of the frontier. They belong to the mesosiderite class. Pieces found near the Cerro de Doña Inez gave, on analysis, the following results:—

	SiO_2.	FeO.	Al_2O_3.	P_2O_5.	NiO.	CoO.	CaO.
I.	18·41	58·96	6·39	0·32	5·28	0·34	3·56
II.	52·87	20·96	7·52	—	0·72	trace	1·67
III.	2·94	75·84	5·89	0·46	7·33	0·48	4·42

	MgO.	S.	Cu.	Total.
I.	4·92	1·06	trace	99·24
II.	14·71	—	—	98·45
III.	0·53	1·54	trace	99·43

(1) Analysis of the mass; (2) analysis of the portion (29·77 per cent.) insoluble in hydrochloric acid; (3) analysis of the portion (70·23 per cent.) soluble in hydrochloric acid. The sp. gr. was 3·98. Under the microscope, the following constituents were detected: red monoclinic and colourless rhombic pyroxene, anorthite, olivine, magnetite, troilite, and nickeliferous iron. B. H. B.

Organic Chemistry.

Substitution in the Aliphatic Series. By V. Meyer and F. Müller (*J. pr. Chem.* [2], **46**, 161—188).—The continuation of the authors' experiments on the halogenation of alkyl halides (this vol., p. 577) shows that the normal course of the reaction must be considered to consist in the attachment of the newly-entering halogen atom to the carbon atom adjacent to the one which carries the already-contained halogen atom, and not to the same carbon atom, as has heretofore been accepted.

A repetition of Tawildarow's experiments (*Annalen*, **176**, 12) showed that ethylidene bromide is almost exclusively produced when the bromination of ethyl bromide is effected at 200°, whereas, as already stated (this vol., p. 577), ethylene bromide is the sole product when the reaction takes place at 100° in the presence of iron wire. The boiling point of ethylidene bromide is 107—108°, not 110—114°, as has been variously stated. The cause of the difference between these reactions was thought to be the spontaneous change of ethylene bromide into ethylidene bromide at 200°; but when ethylene bromide was heated in a sealed tube for 13 hours at this temperature, it was unchanged. Nor could ethylidene bromide be obtained from ethylene bromide by heating it with hydrogen bromide, hydrobromic acid, or bromine. Two other explanations of the reaction at 200° suggest themselves: (1) the ethylene bromide may, at the moment of its formation, decompose into vinyl bromide and hydrogen bromide, which re-combine again to form ethylidene bromide; (2) the change of orientation is similar to such as occurs when toluene, for example, is brominated under different conditions.

The bromination of ethylidene bromide, in the presence of iron, at 70—80°, yields 1 : 1 : 2-tribromethane. The chlorination of ethylidene chloride by antimony pentachloride in a reflux apparatus yields 1 : 1 : 2-trichlorethane (b. p. 111—112°). Ethylene chloride is not attacked by antimony pentachloride in a sealed tube at 100°. Both normal propyl chloride and isopropyl chloride yield propylene chloride (b. p. 96—98°) when treated with antimony pentachloride at normal pressure; in the case of the former, the mixture requires heating at 35—45°, but the reaction takes place at the ordinary temperature in the case of the latter.

The following reactions confirm the authors' views, if the identification of the products be correct. The brominations were effected by bromine in the presence of iron wire in a reflux apparatus at 50—60°, and the chlorinations by antimony pentachloride at the ordinary temperature.

Butyl bromide (1-bromobutane) yields a dibromide which boils at 157° and appears to be identical with pseudobutylene bromide (2 : 3-dibromobutane), in which case a change of orientation on the part of the bromine atom in butyl bromide must occur. The authors have been unable to effect such a change without the substitution by

bromine. *Secondary butyl bromide* (2-bromobutane, b. p. 90—93°) also yields pseudobutylene bromide. Isobutyl bromide (1-bromo-2-methylpropane) yields some isobutylene bromide (1 : 2-dibromo-2-methylpropane, b. p. 148—149°), but higher brominated products predominate. Tertiary butyl bromide (2-bromo-2-methylpropane) also yields isobutylene bromide; the reaction takes place at the ordinary temperature, and the production of higher brominated compounds is much smaller.

The chlorination of normal butyl chloride produces a dichloride which boils at 115—120°, and appears to be 2 : 3-*dichlorobutane*. Isobutyl chloride (1-chloro-2-methylpropane) and tertiary butyl chloride (2-chloro-2-methylpropane) both yield a dichloride which boils at 105—107°, and appears to be 1-chloro-2 : 2-chloromethylpropane; its boiling point agrees with that of d'Oetreppe's dichloride (*Jahresber.*, 1882, 441), and, less exactly, with that of the dichloride which Œconomides obtained by the action of phosphoric chloride on isobutaldehyde (Abstr., 1881, 709). A. G. B.

1 : 3-Dinitropropane. By F. Keppler and V. Meyer (*Ber.*, **25**, 2638).—The authors have obtained small quantities of trimethylenediamine platinochloride by adding glacial acetic acid (40 grams) to an aqueous solution (100 grams) of sodiodinitropropane (7 grams); sodium amalgam (500 grams of 2·5 per cent.) is now gradually added, and the temperature kept below 25° by cooling. The base is separated from the solution by E. Fischer's method (Abstr., 1884, 1289). W. J. P.

Action of Silver Nitrite on Methylene Iodide. By A. Russanow (*Ber.*, **25**, 2635—2637).—Iodonitromethane was obtained by V. Meyer (this vol., p. 575) by the action of silver nitrite on methylene iodide. It is prepared by adding silver nitrite (5 grams) to a solution of methylene iodide (3 grams) in ether (20 c.c.); a trace of iodine is added, the whole carefully heated to boiling for 45 minutes, and then allowed to remain for some hours at the ordinary temperature. The ethereal solution is filtered, and the residue repeatedly extracted with small quantities of ether. Absolute alcohol (1 vol.) is now added to the ethereal solution (1 vol.), and sodioiodonitromethane (0·5—0·8 gram) precipitated by the addition of sodium ethoxide. The precipitate is collected, washed first with a mixture of ether (1 vol.) and absolute alcohol (1 vol.), then with ether, and finally dried over sulphuric acid. The sodium derivative is a slightly hygroscopic, white powder, which explodes on heating and decomposes when kept. Its aqueous solution, acidified with sulphuric acid and extracted with ether, yields iodonitromethane as an oil of pungent odour, which very quickly decomposes, giving free iodine.

The sodium derivative may be diazotised, if great care be employed, by the use of diazo-salts; if excess of the latter be added, however, nitromethane derivatives, containing no iodine, are obtained. Slightly less than the theoretical quantity of diazo-salt is therefore used. Sodioiodonitromethane is dissolved in water (400 parts), and the ice-cold solution (50 parts) of the diazochloride added; the precipitate

is rapidly collected, washed with water, dissolved in a little ethyl acetate, diluted with much alcohol, and precipitated with water. The precipitate should give a carmine solution with concentrated sulphuric acid; if a violet or blue colour is obtained, nitromethane derivatives have been produced. The precipitate, after filtration, is generally pure.

Iodonitromethaneazobenzene, $NO_2 \cdot CHI \cdot N_2Ph$, is obtained by the above method in orange-yellow, microscopic needles. It melts at 110—112° with complete decomposition, and, with concentrated sulphuric acid, gives a carmine solution which soon turns grey.

Iodonitromethaneazotoluene closely resembles the preceding substance; it melts at 108—110°.

If the diazotisation be carelessly performed in a concentrated solution, cherry-red needles of azobenzenenitromethane, or of parazotoluenenitromethane, are respectively obtained. W. J. P.

Silver and Copper Compounds of Acetylene. By E. H. Keiser (*Amer. Chem. J.*, **14**, 285—290).—Acetylene was passed through ammoniacal solutions of cuprous or silver salts respectively. The precipitate was washed by decantation in tall cylinders, from which the air had been removed by a current of carbonic anhydride, using first dilute ammonia, then water, and finally alcohol and ether. It was then drained by the filter-pump and quickly transferred to a vacuum desiccator shielded from the light; the silver compound when dry, was snow-white. Specimens dried at the ordinary temperature contained from 89·31 to 89·44 per cent. of silver; a preparation dried at 100° in a vacuum contained 89·62 per cent. silver. The formula C_2Ag_2 requires 89·99 per cent.; Miasnikoff's formula (*Annalen*, **118**, 330), $C_2H_2Ag_2$, requies 89·25 per cent. of silver.

A weighed quantity exploded in a vacuum yielded but a very small quantity of gas, and that was almost entirely absorbed by potash; the residue consisted of carbon and finely divided silver. The formula C_2Ag_2 may therefore be considered as established.

The copper compound invariably contained free carbon; moreover the voluminous precipitate was usually contaminated with the substances in solution. The best result was obtained by the action of acetylene on cuprous hydroxide suspended in water. The analyses indicate that Cu_2C_2 is the formula of the compound. As in the case of silver, no hydrogen was obtained on explosion.

Compare Plimpton, Proc., 1892, 109. W. T.

Action of Hydrogen Cyanide on Mercurous Salts. By D. Vitali (*L'Orosi*, **15**, 186—192).—Cheynet (*J. Pharm.*, 1892, 456), Fouquet (Abstr., 1890, 229), and others have described experiments to show that in the reaction between hydrogen cyanide and calomel, mercury, mercuric cyanide, and hydrogen chloride are formed. This is further confirmed by the following observations:—

On leaving pure calomel and very dilute hydrocyanic acid in contact for 24 hours, with occasional agitation, the calomel turns ash-

coloured, and the solution becomes strongly acid. This is due to the hydrogen cyanide, as, on adding a few drops to an alcoholic solution of Congo-red, it turns blue; an alcoholic solution of phenolphthaleïn reddened by soda is also decolorised.

The presence of hydrochloric acid is shown by the insolubility of the silver nitrate precipitate in nitric acid, and by the blackening of a silver dish in which a portion of the solution was placed together with a little potassium nitrite.

Mercuric chloride is absent from the solution, as no precipitate is obtained on adding excess of potash. The presence of mercuric cyanide in the solution is proved by expelling the free hydrogen cyanide at a gentle heat, passing hydrogen sulphide, and testing the liquid for hydrogen cyanide.

The absence of mercuric chloride was proved by titrating the solution with standard alkali in presence of phenolphthaleïn, before and after treatment with hydrogen sulphide, the acidity being actually somewhat lower in the latter case. S. B. A. A.

Fulminuric and Deoxyfulminuric Acids. By P. Seidel (*Ber.*, **25**, 2756—2759).—In a former paper (this vol., p. 690), the author described the formation of ethyl fulminurate and of an acid obtained from it by the action of boiling water or alcohol. This acid, *deoxyfulminuric acid*, $C_3H_3N_3O_2$, is best obtained by simply boiling the ethereal salt with water, as, if alcohol is used, further decomposition occurs with evolution of hydrogen cyanide, and the product is less pure. The acid is decomposed by hydrochloric acid at 110—120°. It could not be reconverted into fulminuric acid by the action of nitric acid or iodine solution. Most of its salts are coloured more or less. The *alkali*, *silver*, and *lead* salts are bright yellow, the *copper* salt greenish-black, the *nickel* salt pale-red, the *ferrous* salt violet, and the *ferric* salt pale-orange. The silver salt, $C_3H_2AgN_3O_2$, when precipitated from slightly acid solutions, can be recrystallised from boiling water, but if prepared from neutral or alkaline solutions, it always decomposes with separation of a pale-brown powder.

If, in the preparation of ethyl fulminurate, the heating is continued for some time, a *second ethyl fulminurate* is also formed. This is the principal product if the reaction is carried out at 100°. It crystallises with 1 mol. H_2O in long, colourless needles, melts at 155°, and decomposes above 175°. It is more soluble in alcohol than its isomeride. Both salts are decomposed by hydrochoric acid at 110—120°, and by alcoholic potash. When heated with a chloroform solution of ammonia, the ether of m. p. 133° yields ammonium deoxyfulminurate, whilst the new ether gives *fulminuramide*, $NH_2{\cdot}C_3H_2O_3N_3$. This crystallises in colourless needles insoluble in alcohol or ether, very sparingly soluble in boiling water, slightly more so in cold soda; it melts with decomposition above 250°. Unlike isofulminuramide, it does not give a double salt with ammoniacal copper solution.

Fulminuric acid thus forms two series of ethereal salts, of which the ethyl salt melting at 133° represents the oxy-salts, that melting at 155° the nitrogen salts. L. T. T.

Water of Crystallisation of Barium Thiocyanate. By J. Tcherniac (*Ber.*, **25**, 2627—2629).—Barium thiocyanate is generally stated to crystallise with 2 mols. H_2O; the author finds, however, that the pure crystallised salt has the composition $Ba(SCN)_2 + 3H_2O$, analogous to that of the crystallised thiocyanates of calcium and strontium. Commercial samples of the crystallised barium salt supposed to contain more thiocyanate than corresponds with 3 mols. H_2O are generally strongly contaminated with sodium salts.

Pure anhydrous barium thiocyanate dissolves readily in absolute alcohol, and the solution on concentration in a vacuum deposits transparent needles; these seem to have the composition

$$Ba(SCN)_2 + 2EtOH.$$

Similarly, anhydrous barium thiocyanate (1 part) dissolves in dry methyl alcohol (1·3 parts) with development of heat; on spontaneous evaporation of the solution, beautiful, lustrous, prismatic needles separate, having the composition $Ba(SCN)_2 + 2MeOH$.

W. J. P.

New Thiosulphates. By A. Purgotti (*Gazzetta*, **22**, 416—426).—Organic thiosulphates were prepared by Spring and Legras (Abstr., 1883, 47), who concluded that thiosulphates of saturated radicles are alone capable of existing. The author has, however, succeeded in preparing thiosulphates containing unsaturated groups.

Sodium allyl thiosulphate, $CH_2{:}CH{\cdot}CH_2{\cdot}S_2O_3Na + H_2O$, is obtained as follows:—Sodium thiosulphate and allyl chloride, in molecular proportion, are dissolved in water (2 vols.) and alcohol (1 vol.) respectively. The solutions are mixed, heated on the water-bath in a reflux apparatus for 4—5 hours, and the product evaporated at a temperature not above 50°. The residue is extracted with hot alcohol, and the solution on concentration yields the salt in beautiful laminæ, which are very soluble in water and hot alcohol. Its aqueous solution gives white precipitates with mercuric chloride and silver nitrate solutions, and is decomposed on boiling. When heated with hydrochloric acid, allyl mercaptan is obtained.

Sodium isopropyl thiosulphate, $CHMe_2{\cdot}S_2O_3Na + 3H_2O$, prepared by a method analogous to that above described, forms crystalline scales which are very soluble in water and hot alcohol, sparingly so in cold alcohol. The aqueous solution gives white precipitates with silver nitrate, and mercuric chloride, and, when concentrated, with barium chloride. The *barium* salt, $(CHMe_2S_2O_3)_2Ba + 2H_2O$, separates from its hot aqueous solution in splendid needles or laminæ.

Sodium ethylene thiosulphate, $C_2H_2(S_2O_3Na)_2$, prepared from ethylene chloride, crystallises in scales very soluble in water and in boiling alcohol. The barium salt crystallises in large, lustrous plates.

Sodium hydroxyethyl thiosulphate, $C_2H_4(OH){\cdot}S_2O_3Na$, is obtained by the action of ethylene chlorhydrin on sodium thiosulphate. It crystallises in small, brilliant needles, and is very soluble in hot water and alcohol. Its aqueous solution is decomposed by boiling, and gives a white precipitate with mercuric chloride; with silver nitrate solution no precipitate is obtained in the cold, but on warming the *silver* salt separates in crystalline laminæ.

Barium acetothiosulphate, $CH_2<\begin{matrix}COO\\S_2O_3\end{matrix}>Ba + 2H_2O$, prepared from sodium thiosulphate and sodium chloracetate, forms crystalline crusts and is fairly soluble in hot water; the solution decomposes slowly on boiling. When treated with hydrochloric acid, it yields thioglycollic acid. The *sodium* salt is very deliquescent, and will not crystallise. The *potassium* salt forms minute needles which are very soluble in water. The *silver* salt forms a white precipitate which alters when kept in the dark.

Sodium ethyl acetothiosulphate, $COOEt{\cdot}CH_2{\cdot}S_2O_3Na$, is obtained by heating ethyl monochloracetate (24 grams) dissolved in alcohol (50 grams) with sodium thiosulphate (50 grams) dissolved in water (80 grams). It crystallises from hot alcohol in beautiful monosymmetric crystals, and is very soluble in water, less so in alcohol. The aqueous solution gives white precipitates with mercuric chloride and silver nitrate. The dry salt, on distillation, yields ethyl dithioglycollate. W. J. P.

Optical Properties of Dulcitol and its Derivatives. By A. W. Crossley (*Ber.*, **25**, 2564—2565).—Diacetyldulcitol and tetracetyldulcitol are both optically inactive; the specimens stated by Bouchardat to be active were probably impure. This fact is of importance in the application of the theory of asymmetric carbon atoms to the compounds of the sugar group. J. B. T.

Disappearance of the Multirotation of Sugars in Ammoniacal Solution. By C. Schulze and B. Tollens (*Annalen*, **271**, 49—54).—Solutions of dextrose and of other sugars in concentrated ammonia do not show multirotation, the rotatory power of the freshly prepared solution being practically constant and, as a rule, rather less than that ultimately attained in aqueous solution.

The specific rotatory power of a solution of dextrose in ammonia of sp. gr. 0·924 is $[\alpha]_D = 49{\cdot}82°$ immediately after solution, that of a similar solution of xylose $[\alpha]_D = 14{\cdot}82°$, and that of a similar solution of maltose hydrate $[\alpha]_D = 126{\cdot}1°$; in all three cases, the specific rotatory power is a little lower than the constant value determined in aqueous solution. On keeping the ammoniacal solutions, the specific rotatory power gradually diminishes; in the case of the xylose solution, for example, it was found to be $[\alpha]_D = 5{\cdot}67°$ at the end of the third, and $[\alpha]_D = -5{\cdot}85°$ at the end of the fifth day.

The specific rotatory power of a solution of dextrose hydrate in 5·7 per cent. ammonia is $[\alpha]_D = 47{\cdot}24°$ about 8 minutes after solution when weaker ammonia is used, the specific rotatory power of the freshly prepared solutions gradually increases until, when 0·1 per cent. ammonia is employed, the specific rotatory power becomes normal. Even 0·01 per cent. ammonia has a very marked influence on the birotation of sugars; the specific rotatory power of a solution of dextrose hydrate in 0·01 per cent. ammonia is 49·98° 8 minutes after solution, and becomes normal at the end of 12—15 minutes longer. When the concentration of the ammonia falls to 0·001 per cent., the effect

of the solvent on the birotation of dextrose can no longer be observed with certainty.

As a result of the examination of the following compounds:—dextrose hydrate, xylose, arabinose, galactose, rhamnose, maltose hydrate, levulose, half rotatory lactose, $C_{12}H_{22}O_{11}$, and normal lactose, $C_{12}H_{22}O_{11} + H_2O$, the authors find that the values for the specific rotatory power in 0·1 per cent. ammonia, determined a few minutes after solution, are practically identical with those obtained with aqueous solutions after 20 hours; only in the case of galactose did the difference between the two values amount to almost 1°.

The rotatory power of cane sugar is not influenced by 0·1 per cent. ammonia. F. S. K.

Xylose and its Optical Properties. By C. Schulze and B. Tollens (*Annalen*, **271**, 40—46).—A large quantity of xylose was prepared from chopped wheat-straw by a method similar to that employed by Bertrand (this vol., p. 28); the yield of pure, colourless xylose amounted to about 5 per cent. of the air-dried straw. The rotatory power of the xylose was then determined in aqueous solutions of different concentration, which had been kept for 20—24 hours; the results of the observations are given in a table and are also mapped on a chart. It was found that the specific rotatory power increases continuously from 18·425° to 23·702° as the concentration increases from 9·706 to 61·737 per cent. For solutions containing up to 34·355 per cent., the specific rotatory power may be calculated by the formula $[\alpha]_D = 18{\cdot}095 + 0{\cdot}06986P$ (P = percentage of xylose in solution), and is represented on the chart by a straight line; for solutions containing from 34·355 to 61·737 per cent., the specific rotatory power may be calculated by the formula $[\alpha]_D = 23{\cdot}089 - 0{\cdot}1827P + 0{\cdot}00312P^2$, and is represented on the chart by a straight line, bent slightly upwards with respect to the first line. The above observations were made at 20°, but special experiments showed that the specific rotatory power is practically constant between 15° and 20°, although above 20° the change begins to be appreciable. F. S. K.

The Pentosans of Woody Vegetable Fibre. By C. Schulze and B. Tollens (*Annalen*, **271**, 55—61; compare Abstr., 1889, 480).—The products of hydrolysis of malt which has been used for brewing are xylose and a comparatively small quantity of arabinose; the presence of mannose could not be detected. Both xylose and arabinose are only slowly decomposed by boiling 10 per cent. sulphuric acid, the former being rather less stable than the latter. Quince juice yields xylose on hydrolysis, and probably also dextrose (compare Bauer, this vol., p. 128); luffa gives about 1 per cent. of pure xylose. F. S. K.

Multirotation of Rhamnose and of the Saccharins. By W. Schnelle and B. Tollens (*Annalen*, **271**, 61—67).—A systematic examination of 10 per cent. aqueous solutions of rhamnose, $C_6H_{12}O_5 + H_2O$, at 20° has shown that the specific rotatory power of the sugar is about $[\alpha]_D = -3{\cdot}11°$ immediately after solution, this value gradually becoming less until, after about $9\frac{1}{2}$ minutes, the solution is

optically inactive; the specific rotatory power then gradually increases, and after 66 minutes, a constant value of $[\alpha]_D = 8{\cdot}56°$, or $[\alpha]_D = 9{\cdot}43°$ for anhydrous rhamnose, is attained. Up to about 40 per cent., the concentration of the solution has no appreciable effect on the specific rotatory power; an increase of temperature diminishes the specific rotatory power, the diminution being about 0·035° between 6° and 20°.

Saccharin prepared from dextrose by Kiliani's method also shows multirotation; immediately after solution, the specific rotatory power is $[\alpha]_D = 94{\cdot}2°$ at 20°, but this value falls to $[\alpha]_D = 88{\cdot}7°$ after a lapse of 11 days; the specific rotatory power also decreases as the temperature rises.

The specific rotatory power of isosaccharin, from lactose, is $[\alpha]_D = 62{\cdot}97°$, that of metasaccharin $[\alpha]_D = -46{\cdot}83°$; these two compounds do not show multirotation. F. S. K.

Production of Acetic Acid from Cellulose and other Carbohydrates; Lignocellulose and Ferric Ferricyanide. By J. F. V. Isaac (*Chem. News*, **66**, 39—40).—If cotton cellulose and hydrocellulose, jute-fibre and pine wood, and sugar are acted on by alkali hydroxides within limits of temperature between 120° and 150° and 250° and 350° they yield from 7 to 10 per cent. of their weight of acetic acid; at the lower temperature, the quantity is considerable, and is increased by prolonging the action and by the addition of weak oxidising agents; potassium hydroxide produces more acetic acid than sodium hydroxide.

Jute fibre absorbs even as much as 80 per cent. of its weight of ferric ferricyanide from solutions obtained by adding potassium ferricyanide to ferric chloride, at the same time converting it into Prussian blue.

Freezing point methods of ascertaining molecular weights with Beckmann's apparatus, owing apparently to dissociation, cannot be used for solutions of cellulose acetate, benzoate, and nitrate in acetic acid. D. A. L.

Urea Oxalate. By P. H. Kirkaldy (*Chem. News*, **66**, 52).—Authorities are at variance as to the anhydrous character of urea oxalate, a view which, however, now finds support in the author's determination of carbon, hydrogen, and nitrogen, and experiments in a vacuum over sulphuric acid. D. A. L.

Propylcarbamide and Unsymmetrical Dipropylcarbamide. By F. Chancel (*Compt. rend.*, **115**, 242—243).—*Propylcarbamide* is readily obtained by the action of ammonia on the mixture of propyl iodide and propyl isocyanate resulting from the action of silver isocyanate on propyl iodide. It can be prepared even more easily by merely mixing aqueous solutions of propylamine sulphate and potassium isocyanate; part of the potassium sulphate separates at once, and the remainder can be precipitated by alcohol. The product is identical in both cases. It crystallises in long needles which melt at 107°, dissolve readily in water or alcohol, and are neutral to litmus. When heated with hydrochloric acid in sealed tubes at 160°, propyl-

carbamide yields carbonic anhydride, propylamine hydrochloride, and ammonium chloride. The nitrate and oxalate are very soluble in water, but they do not crystallise well from aqueous solutions; they are also very soluble in alcohol, from which the nitrate crystallises in slender needles.

Unsymmetrical dipropylcarbamide, $NH_2 \cdot CO \cdot NPr_2$, is obtained by mixing aqueous solutions of dipropylamine sulphate and potassium isocyanate. It is very soluble in water and alcohol, and crystallises from the latter in white needles which melt at 57°; it is neutral to litmus. The normal oxalate is very soluble in water, from which it crystallises readily in needles; it is acid to litmus. The nitrate forms an uncrystallisable syrup. C. H. B.

New Method of Preparing Dimethylethylsulphine and Methyl Ethyl Sulphide. By G. Carrara (*Gazzetta*, **22**, 408—415).—Trimethylsulphine may be prepared by heating methyl sulphide (10 parts) with dry iodine (1 part) in a sealed tube at 110—120° for 24 hours; the reaction proceeds more slowly at 110°. No hydrogen iodide is produced. The product is dissolved in water and separated from unattacked methyl sulphide; the aqueous solution, after extraction with carbon bisulphide, is treated with silver chloride, filtered, evaporated on the water-bath, and trimethylsulphine platinochloride precipitated from the alcoholic ethereal solution by the addition of platinum tetrachloride. Methyl bisulphide is also produced in the reaction.

A mixture (10 parts) of ethyl and methyl sulphides in molecular proportion was heated with iodine (1 part) in a sealed tube at 120—140° for 24 hours. By treating the product as above, dimethylethylsulphine platinochloride and trimethylsulphine platinochloride were obtained. The liquid separated from the aqueous solution contained a considerable proportion of methyl ethyl sulphide, which may be obtained pure by fractional distillation.

A mixture of amyl and ethyl sulphides, when heated with iodine at 130—140°, and subsequently treated as above, yields only triethylsulphine platinochloride. Hence, it seems that there is a tendency towards the formation of a sulphine containing as few carbon atoms as possible. No ethyl bisulphide could be detected in the product.

If the additive product of methyl sulphide and bromine, Me_2SBr_2, obtained by Cahours (*Annalen*, **132**, 82), is heated with iodine at 115—120°, and afterwards treated as above, it yields trimethylsulphine platinochloride. W. J. P.

Diethyldithiophosphinic Acid. By A. W. v. Hofmann and F. Mahla (*Ber.*, **25**, 2436—2444).—When diethylphosphine (1 mol.) is added to sulphur (2 atoms), immersed in a small quantity of ether, and the mixture is kept cool, the sulphur readily dissolves, and, after a few hours, crystals separate. When the mother liquor is boiled with a slight excess of aqueous ammonia, more crystals are formed, and are collected while the liquid is hot. The solution as it cools deposits triethylphosphine sulphide, PEt_3S, whilst the cold solution, separated from these and concentrated, yields crystals of *ammonium diethyldithiophosphinate*, PEt_2SSNH_4. The latter melts at 193°, and decomposes at a

slightly higher temperature, but can be sublimed if heated rapidly. It dissolves readily in water and alcohol; its aqueous solution gives amorphous precipitates with silver, lead, and copper salts; in alcoholic solutions, crystalline precipitates are obtained. Calcium and barium salts give no precipitate; soda liberates ammonia. Bromine converts it into diethylthiophosphinic acid. Hydrochloric acid sets free *diethyldithiophosphinic acid*, PEt_2SSH, as an oil which is easily soluble in ether and alcohol, insoluble in and heavier than water, and not volatile with water vapour; it is a strong acid. The *silver salt*, PEt_2SSAg, forms white needles insoluble in cold alcohol, and stable at 100°. The *benzyl derivative*, PEt_2SSBz, melts at 54°, and is insoluble in water, but soluble in most other solvents.

The substance which first separates, after adding diethylphosphine to sulphur, crystallises from carbon bisulphide in hard, white, hexagonal prisms of adamantine lustre, and with rhombohedral faces at the extremities; it melts at 105°, and probably has the composition $PSEt_2{\cdot}S{\cdot}S{\cdot}S{\cdot}PSEt_2$. Freshly prepared ammonium sulphide converts it into ammonium diethyldithiophosphinate, with liberation of free sulphur. C. F. B.

Formaldehyde. By A. Kekulé (*Ber.*, **25**, 2435—2436).—If the gaseous formaldehyde, obtained by heating the dried solid modification, be cooled by a mixture of solid carbonic anhydride and ether, it condenses to a colourless, mobile liquid which boils at −21°, and has approximately the sp. gr. 0·9172 at −80°, and 0·8153 at −20°. At −20° it is transformed in a short time into the solid variety. In a sealed tube at the ordinary temperature the same change takes place, but so rapidly as to cause a considerable rise of temperature and a series of small explosions in the tube. C. F. B.

Preparation of Aldol and Crotonaldehyde. By W. R. Orndorff and S. B. Newbury (*Monatsh.*, **13**, 516—518; compare Abstr., 1891, 285).—To obtain a good yield, the following directions must be closely adhered to:—Aldehyde boiling at 21° is prepared by boiling paraldehyde with a drop of concentrated sulphuric acid, and leading the vapour through a long Hempel's tube packed with glass beads. 200 grams is then cooled to 0°, and gradually added to 200 grams of water at 0°, the temperature not being allowed to rise above 5°. The mixture is then cooled to 0°, and 10 grams of dry, powdered potassium carbonate added in successive small portions, care being taken that no rise of temperature takes place. After the carbonate is all dissolved, the flask is removed from the ice and water and allowed to remain for 12—18 hours in a cool place, preferably at about 10°; the liquid has then become syrupy, and slightly yellowish in colour. It is poured into a separating funnel of 1 litre capacity, and shaken for a long time with an equal volume of ether; the aqueous extract is removed, shaken with half its volume of ether, separated from the same, just neutralised with dilute hydrochloric acid, and again shaken with half its volume of ether. The ether extracts are united, and the ether distilled off; the residue amounts to 90 per cent. of the aldehyde employed, and consists chiefly of aldol, mixed with ether,

aldehyde, paraldehyde, and water. To obtain the aldol, this residue is distilled under diminished pressure. From 100 grams of aldehyde 50 grams of aldol boiling at 90—110° under 40 mm. pressure were thus obtained.

To prepare crotonaldehyde, the residue should be at once distilled under atmospheric pressure over a bare flame, a short Hempel's tube filled with glass beads being used, and the thermometer not being allowed to indicate a temperature higher than 100°. To the distillate calcium chloride is added until the water in it is saturated, and the whole is poured into a separating funnel and shaken, in order to completely remove the water and aldol. The aqueous solution is separated from the crotonaldehyde, which after being dried by boiling it with calcium chloride in a reflux apparatus, is fractionated in a distilling flask, the neck of which is filled with glass beads. From 200 grams of aldehyde, 48—50 grams of pure crotonaldehyde, boiling at 104—105°, were thus obtained. C. F. B.

Preparation of Crotonaldehyde. By A. Lieben (*Monatsh.*, **13**, 519—521; see also preceding abstract).—50 c.c. of acetaldehyde are placed in a sealed tube with 10 c.c. of a 28 per cent. aqueous solution of sodium acetate; the tube is shaken, and then heated for about 36 hours in a horizontal position at 95—100°. The contents have then contracted to about seven-eighths of their original volume, and the upper layer should have a slight, but only a slight, yellowish tinge. The contents, after being distilled on the water-bath to remove acetaldehyde, are distilled with steam, when oily drops of crotonaldehyde and other substances come over. These are fractionated in an atmosphere of carbonic anhydride, preferably under reduced pressure, so that the temperature does not exceed 130°. From 100 parts of acetaldehyde, 30 parts were recovered, and 42 parts obtained volatile with steam; of these, 21 were crotonaldehyde. C. F. B.

Glycolaldehyde. By E. Fischer and K. Landsteiner (*Ber.*, **25**, 2549—2554).—Bromacetal is readily prepared by the action of bromine (136 grams) on acetal (100 grams) in presence of recently precipitated calcium carbonate (42 grams), a product being obtained which boils at 164—172°; the yield is 50 per cent. The bromacetal is then heated with the calculated quantity of anhydrous oxalic acid at 150°, and the distillate fractionated; the portion boiling at 80—105° consists of bromaldehyde together with water and some impurities; this mixture forms a colourless, viscid liquid, which is soluble in water, and readily reduces alkaline copper solution; the vapour rapidly attacks the eyes. On treatment with phenylhydrazine in aqueous solution, an insoluble compound is formed which has not been further investigated.

Glycolaldehyde is prepared from the preceding impure bromocompound by treatment with barium hydroxide in aqueous solution at 0°; the aldehyde readily reduces alkaline copper solution at ordinary temperatures, and turns yellow on warming with alkalis; it is insoluble in ether, and is only very slightly volatile with steam either

at ordinary pressures or in a vacuum. On heating the aldehyde with phenylhydrazine acetate at 40°, glyoxalphenylosazone is formed.

Glycolaldehyde, like ordinary sugars, is oxidised to glycollic acid by the action of bromine water. On treating the aqueous solution of glycolaldehyde (see above) with soda, in such quantity that the liquid contains 1 per cent., it undergoes polymerisation; after remaining 15 hours at 0°, the liquid no longer reduces alkaline copper solutions at ordinary temperatures; and on heating with phenylhydrazine acetate for 8—10 hours, a compound is deposited which melts at 166—168°, and appears to be identical with phenylerythrosazone; attempts to regenerate the sugar from this compound were unsuccessful.

With the synthetic formation of tetrose, a complete series of sugars as far as the nonoses is known, and all can be prepared synthetically with the exception of the pentoses. J. B. T.

Chloracetone. By J. Tcherniac (*Ber.*, **25**, 2629—2632; compare following abstracts).—When crude thiocyanacetone is distilled with water in a vacuum, an oil passes over, which can be only partially separated into two substances by fractional distillation. On treating it with hydrogen sodium sulphite solution, a considerable proportion dissolves, and when recovered by distilling the aqueous solution with the calculated quantity of calcium chloride, is found to be pure dichloracetone; this has a slightly pungent but not ethereal odour, more like that of chloral than of chloracetone. It thus differs from the descriptions given by Chlöez (*Ann. Chim. Phys.* [6], **9**, 165), and by Borsche and Fittig (*Annalen*, **133**, 111). The oil insoluble in the sulphite solution, on extraction with ether and evaporation of the ethereal solution, yields a mixture boiling at 123—125°. Its approximate composition is C_5H_9ClO, and it seems to be the constituent which gave to Borsche and Fittig's chloracetone its pleasant ethereal odour.

These two components of the oil must have been originally present as impurities in the chloracetone used in the preparation of the thiocyanacetone; it would therefore seem that chloracetone obtained by Barbaglia's method contains at least 15 per cent. of foreign matter. Halogen determinations in chloracetone prepared in this way, however, agree with the formula C_3H_5ClO. W. J. P.

Thiocyanacetone. By J. Tcherniac (*Ber.*, **25**, 2607—2620).—Tcherniac and Hellon (Abstr., 1883, 653) obtained an oil which they considered to be thiocyanacetone by the action of barium thiocyanate on chloracetone. Hantzsch and Weber (Abstr., 1888, 256), by slightly modifying their method of preparation, obtained only a crystalline substance which they termed methyloxythiazole. Later, however, Arapides (Abstr., 1889, 413) stated that thiocyanacetone is produced in the reaction, but cannot be isolated in a pure state, as in presence of water it is slowly converted into its isomeride, methyloxythiazole.

Thiocyanacetone dissolves in aqueous hydrogen potassium sulphite with considerable development of heat, thus indicating its ketonic

nature. The author finds that the method given by Arapides for its preparation is not only costly but yields an impure product; he was quite unable to effect the conversion of thiocyanacetone into methyloxythiazole, as described by Arapides. Thiocyanacetone cannot be converted into the thiazole by heating its aqueous solution on the water-bath with dilute hydrochloric acid; the thiazole is also but slightly soluble (12 per cent. at 14°) in the acetone.

Hantzsch and Weber, in preparing methyloxythiazole, added dry sodium carbonate to the solution, and then obtained no thiocyanacetone; the author finds that the acetone is converted into methyloxythiazole not only by sodium carbonate, but by such slightly alkaline substances as borax, normal sulphites, and zinc oxide. This affords an explanation of Hantzsch and Weber's erroneous statement that no thiocyanacetone is formed.

The author considers that he has proved that the oil obtained by himself and Hellon is the true thiocyanacetone, and under normal conditions contains no methyloxythiazole. W. J. P.

Preparation and Estimation of Thiocyanacetone. By J. Tchernjac (*Ber.*, **25**, 2621—2626).—The author has devised a thermoanalytical method of estimating thiocyanacetone. The heat developed on treating an aqueous solution of this substance with normal sodium carbonate solution is directly proportional to the amount of the acetone present. The estimation is carried out in a Beckmann's apparatus for cryoscopic determinations, and is performed in much the same way as those determinations.

The author prepares thiocyanacetone as follows:—Equivalent quantities of chloracetone and crystallised barium thiocyanate are shaken together in a thick flask containing some glass marbles to break up the mass. The odour of chloracetone disappears after 6—15 hours, when the reaction is complete. The product is extracted thrice with ether, the ethereal solution washed with a little water, and distilled at 40—50°. A slow stream of carbonic anhydride is passed through the residue, kept under a low atmospheric pressure at 40—50°; after evaporating off the water by this means, the residual oil contains about 98·18 per cent. of thiocyanacetone. It can be further purified by shaking its saturated aqueous solution in the cold with animal charcoal (1 per cent.); on extracting with ether, and evaporating the ethereal solution in a vacuum over sulphuric acid, a product containing 99·18 per cent. of thiocyanacetone is obtained. On distilling the aqueous solution of this under reduced pressure in a stream of carbonic anhydride at 40—50°, and evaporating the ethereal extract of the distillate in a vacuum over sulphuric acid, a still purer product is got.

Thiocyanacetone, prepared as above, is a slightly coloured, strongly refractive oil, which darkens very slowly when kept in the dark. Its sp. gr. is 1·200 at 0°/4° and 1·180 at 20°/4°. It dissolves in 14·3 parts of water at 15°, and is very soluble in ether, benzene, and chloroform, sparingly so in light petroleum and carbon bisulphide; it is fairly stable towards dilute acids. W. J. P.

Stereometric Relations of Erucic Acid and Brassidic Acid. By A. Holt (*Ber.*, **25**, 2667—2671).—In a previous paper (this vol., p. 812), the author has shown that the bromo- and iodo-additive products of behenolic acid are reconverted into behenolic acid by the action of sodium amalgam, and are therefore to be considered as derivatives of brassidic acid. The present paper deals with the chloro-additive compounds.

Dichlorobrassidic Acid.—When a chloroform solution of behenolic acid cooled with ice and salt is treated with chlorine, 1 mol. of chlorine is absorbed, and a viscid, pale-yellow oil is obtained, which gives numbers corresponding with the formula of dichlorobrassidic acid. On treating this product with sodium amalgam, it is found to be a mixture, for it yields a small quantity of behenolic acid, an oil free from chlorine, and a small quantity of behenic acid (m. p. 76°). Dichlorobrassidic acid is, however, easily obtained in a state of purity by boiling the corresponding dibromo-componnd with mercuric chloride (1 mol.) in alcoholic solution. It is a viscid, bright yellow oil, is somewhat sparingly soluble in cold alcohol, easily so in warm alcohol and other organic solvents, and when treated with sodium amalgam yields 90 per cent. of the theoretical quantity of behenolic acid.

The *tetrachloride of behenolic acid* cannot be obtained by the direct action of chlorine on behenolic acid; but is easily obtained by boiling the tetrabromide with mercuric chloride (2 mols.). It separates from alcohol as an oil, but soon solidifies in beautiful, long needles; it melts at 41°, and when treated with sodium amalgam is entirely converted into behenolic acid.

Behenolic acid dissolves in pure concentrated sulphuric acid to a pale-brown, clear solution, which yields a small quantity of precipitate after a time, and darkens. By pouring the product into water, a hydroxy-acid, $C_{22}H_{41}O_2{\cdot}OH$, is obtained; this crystallises from alcohol as a white powder, melts at 83°, and is identical with the acid obtained by the action of concentrated hydrochloric acid on behenolic acid.

Behenolic anilide, $C_{21}H_{39}{\cdot}CO{\cdot}NHPh$, is obtained by heating behenolic acid with excess of aniline for four hours at 220°, and extracting the product with very dilute hydrochloric acid. It separates from alcohol as a colourless, voluminous, crystalline mass, melts at 73°, is easily resolved into its components by halogen acids, is fairly stable towards potash, and when boiled with alcoholic potash for 10 hours yields aniline and behenolic acid.

Behenolic phenylhydrazide, $C_{21}H_{39}{\cdot}CO{\cdot}NH{\cdot}NHPh$, is obtained by warming molecular proportions of behenolic acid and phenylhydrazine at 140—145°. It crystallises from alcohol in small, colourless needles, melts at 86·5°, is somewhat sparingly soluble in cold alcohol, gives a mirror with alcoholic ammoniacal silver nitrate, and dissolves in concentrated sulphuric acid to a colourless solution, which turns dark-red on the addition of potassium dichromate. When oxidised with copper acetate in alcoholic solution, it yields behenolic acid and *behenolic diphenylhydrazide*, $C_{21}H_{39}{\cdot}CO{\cdot}NH{\cdot}NPh_2$; this melts at 104—105°, and with sulphuric acid gives a bluish-green solution which turns pure blue on the addition of potassium dichromate.

The author has also prepared the phenylhydrazides of erucic, brassidic, and stearolic acids, by heating the acids with phenylhydrazine in molecular proportion at 140°.

Stearolic phenylhydrazide crystallises in lustrous, white needles, melts at 81·5—82°, and with sulphuric acid gives a bright yellow solution, which changes to rose-red on the addition of potassium dichromate.

Erucic phenylhydrazide is a white, crystalline powder, melts at 82°, and gives a colourless solution with sulphuric acid, which on the addition of potassium dichromate changes to blood-red and then brown.

Brassidic phenylhydrazide is a white, crystalline mass, melts at 95°, and gives the same colour reactions with sulphuric acid as the preceding compound. E. C. R.

Constitution of Ethyl Sodacetoacetate. By A. Michael (*J. pr. Chem.* [2], **46**, 189—208).—The author continues his criticism (this vol., p. 1178) of Nef's paper on ethyl acetoacetate (this vol., p. 140). From the fact that ethyl copper acetoacetate and ethyl lead acetoacetate do not react so easily with ethyl iodide as ethyl sodacetoacetate does, Nef argues that there is no direct substitution of the sodium by the ethyl in the latter reaction, and in support of this he quotes what he supposes to be facts concerning the greater ease with which copper, lead, or mercury phenol, and the salts of these metals, are attacked by ethyl iodide than are the corresponding sodium compounds. The author asserts that this difference is entirely imaginary. According to Nef's hypothesis, an intermediate compound containing the group :CI·ONa is formed when ethyl iodide and ethyl sodacetoacetate react. The iodine atom in this group is then supposed to leave the molecule in company with the hydrogen atom of the next group; the group CONa remains, and subsequently reacts with the evolved hydrogen iodide, forming the group COH. This is contrary to all our knowledge concerning compounds which contain both hydroxyl and halogen atoms attached to the same carbon atom; such compounds lose the hydroxyl hydrogen and halogen as hydrogen halide with the greatest ease, and the same course of change may surely be expected when sodoxyl replaces hydroxyl. Nor can Nef's experiments be held to fully confirm his conclusion that the more negative the group introduced into the molecule of ethyl acetoacetate the larger will be the proportion of di-substitution product formed in subsequent reactions (this vol., p. 141). For inasmuch as the reaction between ethyl chlorocarbonate and ethyl sodacetoacetate results in the production of 7 parts of di- and 2 parts of mono-derivative (ethyl acetylmalonate and ethyl acetylcarbintricarboxylate, this vol., p. 145), acetyl must be, according to Nef, more negative than the group COOEt, yet the reaction between ethyl sodacetoacetate and acetic chloride yields much ethyl acetylacetoacetate and only a little ethyl diacetylacetoacetate (ethyl triacetylacetate, this vol., p. 145). The statement that ethyl ethylacetoacetate is not reduced by treatment with sodium in ethereal solution is incorrect; the author found that the quantity of hydrogen evolved by the reaction is far short of

the theoretical quantity, and when the liquid was subsequently examined undoubted evidence of the presence of unsaturated acids was obtained.

These are the main points of the critical portion of the paper. The theoretical considerations with which it concludes can only be appreciated by reference to the original. A. G. B.

Action of Phenylhydrazine and of Hydroxylamine on Dehydrodiacetyllevulinic Acid. By G. Magnanini and M. Scheidt (*Gazzetta*, **22**, 436—448).—An *oxime* of dehydrodiacetyllevulinic acid, $C_9H_{11}NO_4$, is obtained when a mixture of the acid (1 gram), hydroxylamine hydrochloride (0·70 gram), and sodium carbonate (1·5 grams) is dissolved in water and left for 24 hours at the ordinary temperature. The oxime is deposited on adding hydrochloric acid, and crystallises from boiling alcohol in colourless needles which melt with decomposition at 198—199°. It is insoluble in water, very soluble in alcohol, and sparingly so in chloroform, benzene, and acetic acid; it decomposes on boiling with water or aqueous alcohol..

Dehydrodiacetyllevulinic acid yields a *hydrazone*, $C_{15}H_{16}N_2O_3$, when heated with phenylhydrazine in acetic acid solution. It forms matted white needles, melts at 185—187°, and is soluble in alcohol and ether, sparingly so in benzene, and insoluble in water. It must be crystallised from absolute alcohol, as it is partially decomposed if heated in presence of water. On heating the hydrazone (1 gram) in a sealed tube with water (25 grams) for 3—4 hours at 150—160°, small, monosymmetric prisms ($a : b : c = 3·4969 ; 1 : 3·8391$, $\beta = 52° 11'$) are obtained, which have the composition $C_{14}H_{16}N_2O$, and melt at 137°. Both this substance and the hydrazone give normal molecular weights by the cryoscopic method.

Attempts to introduce a second phenylhydrazine residue into dehydrodiacetyllevulinic acid were unsuccessful. When the acid is heated with phenylhydrazine, water, and acetic acid at 200°, a substance of the composition $C_{14}H_{16}N_2O$ is obtained.

On heating dehydrodiacetyllevulinic acid in a sealed tube with ammonia at 100°, a substance of the composition $C_8H_{11}NO$ is formed; this, on treatment with benzaldehyde, gives a compound which has the composition $C_{15}H_{15}NO$, and crystallises in small, orthorhombic prisms ($a : b : c = 2·3333 : 1 : 1·9301$). It is soluble in alcohol and chloroform, less so in acetic acid, and insoluble in water; it melts at 208·5°, and gives a normal molecular weight by the cryoscopic method. The compound $C_8H_{11}NO$ gives a chloride and a platinochloride, and readily combines with bromine; when either this substance or the compound obtained by treating it with benzaldehyde is distilled with zinc-dust, oils are obtained which have the properties of pyrrolines. These two substances are now under investigation.

The authors have determined the electrical conductivity of dehydrodiacetyllevulinic acid, $K = 0·00682$. If the solution is kept, the coefficient changes rapidly, owing to decomposition of the acid.

W. J. P.

Azodicarboxylic Acid. By J. Thiele (*Annalen*, **271**, 127—136).—Hydrazodicarbonamide (compare this vol., p. 1295) is best pre-

pared by dissolving hydrazine sulphate (130 grams) and crystallised sodium acetate (136 grams) in warm water (about 1·3 litres), and adding to the cold mixture a concentrated solution of potassium cyanate (180 grams). After a short time, the separation of hydrazodicarbonamide commences, and the solution, which would otherwise become feebly alkaline, is kept slightly acid by the addition of acetic acid. After about two hours time, a further quantity (25—30 grams) of potassium cyanate is added, and the solution allowed to remain over night; the colourless crystalline product is then separated by filtration, washed, and dried. The yield is 103 grams, or 87 per cent. of the theoretical.

Hydrazodicarbonamide seems not to be acted on by moderately concentrated (1 : 1) potash in the cold; it is soluble in warm potash, yielding as a rule a turbid solution, from which it is precipitated unchanged on adding water. Azodicarbonamide (*loc. cit.*) can be easily obtained by triturating the finely-divided hydrazo-compound (10 grams) with water (1 litre), heating to boiling, and then adding a solution of potassium dichromate (16 grams) in water (60 c.c.) and sulphuric acid (15 c.c.); an energetic reaction takes place, the mixture darkens in colour, and the whole of the hydrazo-compound passes into solution. The solution is then cooled to 0° as quickly as possible, and the azodicarbonamide, which is precipitated as an orange-red powder, separated by filtration, washed, and dried. The yield is 70 per cent. (7 grams). Azodicarbonamide is decomposed by boiling sodium carbonate, yielding nitrogen, carbonic anhydride, ammonia, and hydrazodicarbonamide.

Potassium azodicarboxylate, COOK·N:N·COOK, is formed with evolution of ammonia when azodicarbonamide is triturated with ice-cold, moderately concentrated (1 : 1) potash. It is a yellow powder, stable in the air, but decomposed by water, in which it dissolves freely with a yellow coloration. The dry substance decomposes slowly at 100°, and explodes at a slightly higher temperature, yielding in both cases potassium carbonate, nitrogen, and carbonic oxide. It gives Liebermann's reaction, but the colorations are much less intense than in the case of a nitroso-compound.

Barium azodicarboxylate, $C_2N_2O_4Ba$, can be obtained by adding a solution of barium chloride, which has been saturated with barium hydroxide, to a solution of the potassium salt; it is a light yellow powder insoluble in water, by which it is quickly decomposed.

When potassium azodicarbonamide is treated with water at the ordinary temperature, a vigorous evolution of nitrogen and carbonic anhydride takes place and a yellow solution is obtained; after a very short time, the solution becomes colourless, and then contains hydrazine and potassium carbonate. The decomposition of the barium salt takes place more slowly, but in a similar manner. The aqueous solution of the potassium salt is much more stable in presence of caustic alkalis, and under these conditions the yellow colour does not disappear for some minutes even on boiling.

All attempts to prepare diimide, NH:NH, from the salts of azodicarboxylic acid were unsuccessful, and it would seem that this compound is incapable of existence. F. S. K.

Copper Oxalate and Cuprammonium Oxalate. By K. Seubert and G. Rauter (*Ber.*, **25**, 2821—2825).—Copper oxalate was prepared by precipitating a solution of copper sulphate with sodium oxalate, and purified by dissolving the finely-divided precipitate in ammonia and pouring the solution into dilute acetic acid. When dried in the air, it contains a little less than 1 mol. H_2O; when dried over sulphuric acid, or by heating at 80—90°, it has the formula $CuC_2O_4 + \frac{1}{2}H_2O$. When dried at 95—105°, it contains $\frac{1}{4}$ mol. water, which cannot be driven off without decomposing the salt.

Cuprammonium oxalate is obtained by the evaporation of a solution of copper oxalate in excess of ammonia. It is decomposed by water at the ordinary temperature with separation of cupric oxalate, and, on boiling, with separation of black cupric oxide. When exposed to air, it decomposes, and all the water and part of the ammonia are given off. The loss in weight is 20·33 per cent. On analysis, the salt gave numbers agreeing with those required by the formula $CuC_2O_4,2NH_3 + 2H_2O$.

A compound of cupric oxalate and pyridine is obtained by rubbing dry copper oxalate with pyridine, and is a crystalline powder. It smells strongly of pyridine, and loses pyridine on exposure to air or on gently heating. When heated at 130°, it decomposes, and when heated strongly, burns with a sooty, green-bordered, yellow flame. The salt has the composition $CuC_2O_4,2C_5NH_5$. E. C. R.

Inactive Ethyl Malate. By W. Wislicenus (*Ber.*, **25**, 2448—2449).—When ethyl oxalacetate, $COOEt{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, is reduced rapidly with sodium amalgam in a cooled acid solution, both inactive malic acid and its ethyl salt are formed. By nearly neutralising the product with soda and extracting with ether, the ethyl salt is removed, and the acid remains behind. The yield of the ethyl salt is about half the amount of the oxalacetate employed. Ethyl malate boils at 150—152° under 27 mm. pressure, and, unlike the acid itself, boils without decomposition under atmospheric pressure, at 255°. It has sp. gr. 1·124 at 21°/4°, and gives an acid reaction with moistened litmus paper. When hydrolysed with soda, it yields the sodium salt as a white, deliquescent, crystalline powder. C. F B.

Polarisation Phenomena of Rhamnonic Acid and Rhamnolactone. By W. Schnelle and B. Tollens (*Annalen*, **271**, 68—74; compare Abstr., 1891, 43).—The specific rotatory power of rhamnonic acid, in a freshly-prepared solution, obtained by decomposing strontium rhamnonate with hydrochloric acid, is about $[\alpha]_D = -7{\cdot}67°$; after keeping for $3\frac{1}{2}$ hours, the specific rotatory power has increased to $[\alpha]_D = -29{\cdot}21°$, at which value it remains; if, however, the solution is heated at 100° for half an hour, the specific rotatory power becomes $[\alpha]_D = -34{\cdot}30°$, the acid being now almost completely converted into the lactone; the specific rotatory power of the solution of the lactone then slowly decreases, owing to partial reconversion into the acid, and after three days' time it has again fallen to $[\alpha]_D = -30{\cdot}12°$. F. S. K.

Polarisation Phenomena of Gluconic Acid and Gluconolactone. By W. Schnelle and B. Tollens (*Annalen*, **271**, 74—80; compare Abstr., 1891, 43, and Fischer, Abstr., 1890, 1389).—The specific rotatory power of the lactone of gluconic acid is $[\alpha]_D = 61{\cdot}59°$ 10 minutes after solution, but this value gradually diminishes, becoming constant at $[\alpha]_D = 20°$ after about a month and a half; from these results, and from those obtained with gluconic acid (*loc. cit.*), it follows that in aqueous solution the lactone is slowly converted into the acid, and *vice versâ*, until a condition of equilibrium is established.

If, in preparing gluconic acid from dextrose, only the theoretical quantity of bromine is employed, there is formed a crystalline lactone, which melts at 110—115°, and seems to have the composition $C_{12}H_{22}O_{11}$ or $C_{12}H_{20}O_{11}$. This substance loses approximately $1\frac{1}{2}$ mols. H_2O at 100°; its specific rotatory power is $[\alpha]_D = 39{\cdot}07°$ immediately after solution, but gradually falls to $[\alpha]_D = 14{\cdot}84°$. F. S. K.

Polarisation Phenomena of Galactonic Acid and Galactonolactone. By W. Schnelle and B. Tollens (*Annalen*, **271**, 81—86; compare Abstr., 1891, 43).—Calcium galactonate, $(C_6H_{11}O_7)_2Ca + 5H_2O$, loses 4 mols. H_2O on long exposure to the air, and becomes anhydrous when gradually heated in a stream of dry air; it crystallises in microscopic plates, is only sparingly soluble (0·76 part in 100) in water at 15°, and its specific rotatory power is approximately $[\alpha]_D = 2{\cdot}85°$. When the calcium salt is decomposed with oxalic acid, and the filtered solution evaporated over sulphuric acid, a crystalline compound melting at 123—125° is gradually deposited; if, however, the filtered solution is concentrated to a syrup, then taken up with warm alcohol, and evaporated over sulphuric acid, the lactone *hydrate*, $C_6H_{10}O_6 + H_2O$, crystallises from the solution; this compound melts at 64—65°, and loses its water at 85°, the anhydrous lactone melting at 90—92°. The specific rotatory power of the lactone hydrate is approximately $[\alpha]_D = -65°$, 10 minutes after solution; this value diminishes slightly on keeping the solution for a long time. F. S. K.

"Isarabic Acid." By M. Conrad (*Ber.*, **25**, 2446—2448).—The formation of this acid, by the action of ferrous sulphate on tartaric acid, is not due, as Ballo thought (Abstr., 1889, 693), to the reducing action of the former, but rather to its dehydrating action (*cf.* Scheibler, this vol., p. 1180). Equal weights of tartaric acid and ferrous sulphate were dissolved in twice the weight of water, and heated on the water-bath for 15 hours. The solution was filtered, concentrated to a small bulk, and extracted with alcohol. The extract was neutralised with barium carbonate, filtered, evaporated to dryness, dissolved in water, and converted, by means of potassium carbonate, into the potassium salt of isarabic acid. The concentrated solution of the latter, when treated with excess of acetic acid and alcohol, gave a precipitate of potassium hydrogen tartrate, and potassium hydrogen isarabate remained in solution. If, however, the latter is precipitated with lead acetate, the precipitate decomposed with hydrogen

sulphide, and the solution filtered and concentrated, tartaric acid crystallises out; if the aqueous solution of the potassium salt is heated for a few minutes only with aqueous potash, and then acidified with acetic acid, potassium hydrogen tartrate separates out. This very ready conversion of isarabic into tartaric acid renders it improbable that the former is formed from the latter by reduction.

C. F. B.

Thetincarboxylic Acids. By A. Delisle (*Ber.*, **25**, 2450—2453).—Dimethylthetin-mono- and -di-carboxylic acids may easily be prepared by digesting a mixtnre of sodium thiodiacetate or methyl thioacetate with sodium chloracetate, in molecular proportion, on the water-bath, and adding hydrochloric acid and ether to the product.

Dimethylthetindicarboxylic acid, $CO<^{O-}_{CH_2}>S(CH_2\cdot COOH)_2$, forms small, colourless, ill-defined, lustrous needles, melts with decomposition at 157—158°, dissolves fairly readily in hot, very sparingly in cold water, and not at all in most organic solvents. It dissolves in concentrated hydrochloric acid, forming the compound $C_6H_8O_6S,HCl$, which, however, easily splits into chloracetic and thiodiacetic acids. When reduced with sodium amalgam, it yields acetic and thiodiacetic acids. When distilled, it breaks up into methyl sulphide, methyl methylthioacetate, and methyl thiodiacetate. The *silver salt*, $C_6H_6O_6SAg_2$, crystallises in needles or plates, and is very stable. The *barium salt*, $C_6H_6H_6SBa$, crystallises in long, radiating, silky needles. The *sodium salt*, $C_6H_6O_6SNa_2 + 3H_2O$, crystallises in brilliant, prismatic needles, readily soluble in water, but insoluble in alcohol. No acid salts have been prepared; salts of alkaline reaction, however, derived from the acid $OH\cdot S(CH_2\cdot COOH)_3$, have been obtained.

Dimethylthetincarboxylic acid, $CO<^{O-}_{CH_2}>SMe\cdot CH_2\cdot COOH$, crystallises in lustrous, slightly opalescent, cubical crystals, and melts with decomposition at 150°.

Pyridinebetaïne may also be obtained by heating pyridine with sodium chloracetate; it forms large, rhomboidal tables.

C. F. B.

Formation of Furfuraldehyde from Glycuronic Acid Derivatives and from Albumin. By A. Günther, G. de Chalmot, and B. Tollens (*Ber.*, **25**, 2569—2572).—Glycuronic anhydride, euxanthic acid, and urochloralic acid, all yield furfuraldehyde on distillation with hydrochloric acid; the proportion of furfuraldehyde from glycuronic acid is almost the same as that obtained from arabinose and xylose.

Normal urine yields a trace of furfuraldehyde on distillation with hydrochloric acid, as also does caseïn and dried horseflesh, which has been freed from carbohydrates.

J. B. T.

Oximes of Furfuraldehyde, Thiophenaldehyde, and Œnanthaldehyde. By H. Goldschmidt and E. Zanoli (*Ber.*, **25**, 2573—2596).—Furfursynaldoxime, $^{C_4OH_3\cdot C\cdot H}_{\quad\quad\quad

by the action of hydroxylamine on furfuraldehyde, or by treatment of the antialdoxime (see below) with hydrogen chloride in ethereal solution; its molecular weight determined by the boiling point method agrees with the above formula. On treating the aldoxime with methyl iodide and sodium methoxide in methyl alcoholic solution, a *methyl derivative* is obtained which crystallises from ether with 1 mol. H_2O in flat, lustrous, transparent needles melting at 56°; after remaining in a vacuum over sulphuric acid for some days, the *anhydrous compound*, $C_4OH_3{\cdot}CH{<}\overset{O}{\underset{NMe}{|}}$, is formed; this crystallises from chloroform, benzene, or ether in large, quadratic, transparent plates, melts at 91—92°, and combines directly with hydrogen chloride; on heating with dilute sulphuric acid, it is resolved into furfuraldehyde and β-methylhydroxylamine.

Two benzylfurfuraldoximes have been described by Werner (Abstr., 1890, 1266) melting at 88° and 65° respectively; the second of these proves to be a hydrate of the first, into which it is converted by remaining for some time over sulphuric acid in a vacuum.

Two isomeric additive compounds are formed by the action of phenyl cyanate on furfursynaldoxime in ethereal solution; the first is deposited in pale yellow, transparent, microscopic, oblique prisms which soften at 65°, melt at 72° with decomposition, and yield diphenylcarbamide, aniline, furfursynaldoxime, and furfurcarboxylic acid on treatment with soda. The second compound is obtained with more concentrated solutions at somewhat higher temperatures, and crystallises in colourless, hexagonal plates melting at 83°; after repeated crystallisation, it is deposited in lustrous, thick prisms which melt at 98°, and yields the same decomposition products with soda as the yellow substance, but on boiling with alcohol or on treatment with acetic chloride at ordinary temperatures, carbanilidofurfurantialdoxime, $\overset{C_4OH_3{\cdot}C{\cdot}H}{\underset{NHPh{\cdot}COO{\cdot}N}{||}}$ (m. p. 138°), is formed.

Carboparatoluidofurfursynaldoxime, $\overset{C_4H_3O{\cdot}C{\cdot}H}{\underset{N{\cdot}O{\cdot}CONH{\cdot}C_6H_4Me'}{||}}$, is prepared from the aldoxime and paratolyl cyanate, and is deposited in pale yellow, transparent plates melting at 79—80° with decomposition; with soda, it decomposes in a similar manner to the phenyl derivative. On recrystallisation from warm ether, a compound is deposited in crystalline plates which melt at 96°. The *orthotoluido-derivative* closely resembles the para-compound, but is more readily soluble, and melts at 50° without decomposition; on crystallisation from absolute alcohol, colourless needles are obtained which melt at 65°.

Furfurantialdoxime, $\overset{C_4OH_3{\cdot}C{\cdot}H}{\underset{HO.N}{||}}$, is prepared by mixing sodium hydroxide (31·4 grams) in water (200 c.c.) with hydroxylamine hydrochloride (11 grams) dissolved in water (50 c.c.); the solution is well cooled, and to it is gradually added furfuraldehyde (10 grams); carbonic anhydride is now passed through it until the soda is neutralised, and the liquid is then extracted with ether; the ether is evaporated, and the residue, after repeated crystallisation from light

petroleum, is obtained in long, colourless, strongly-refractive needles melting at 73—74°. Molecular weight determinations by the boiling point method confirm the above formula. The compound is soluble in ether, benzene, alcohol, and water; on heating with dilute sulphuric acid, it is resolved into its constituents. The isomeric furfuraldoxime (m. p. 49—56°) described by Oderheimer consists of a mixture of furfursynaldoxime and antialdoxime, as is shown by its action on phenyl cyanate. With orthotolyl or paratolyl cyanate, carbotoluidofurfursynaldoximes (see below) are formed, the anti-derivatives being apparently incapable of separate existence.

Benzantialdoxime, on treatment with paratolyl cyanate in ethereal or benzene solution, both at ordinary temperatures and on warming, yields *carboparatoluidobenzantialdoxime*, $\begin{matrix}C_6H_5\cdot C\cdot H\\ \|\\ C_6H_4Me\cdot NH\cdot COO\cdot N\end{matrix}$, which crystallises from benzene in colourless needles and melts at 121°. The corresponding *benzsynaldoxime derivative* melts at 74—76°, and on recrystallisation from ether is converted into a compound which melts at 88—89°.

Furfurantialdoxime is partially converted into the synaldoxime by the action of acetic anhydride; on treatment with methyl iodide in the manner above described and distilling with steam, a product is isolated which boils at 150—168°, and appears to be an impure *methyl* ether; methylfurfursynaldoxime is also produced in considerable quantity.

Thiophenaldoximes.—Thiophensynaldoxime melts at 133°, instead of 128°, as stated by V. Meyer. On treatment with methyl iodide, it yields *methylthiophensynaldoxime*, $C_4SH_3\cdot CH<\begin{matrix}NMe\\ |\\ O\end{matrix}$, which crystallises from benzene in thin, transparent plates melting at 120°. It combines directly with hydrogen chloride, and, on boiling with dilute sulphuric acid, is resolved into thiophenaldehyde and β-methylhydroxylamine, whilst heating it with hydriodic acid at 100° gives rise to methylamine. Thiophensynaldoxime combines with phenyl cyanate in ethereal solution to form *carbanilidothiophensynaldoxime*, $\begin{matrix}C_4H_3S\cdot C\cdot H\\ \|\\ N\cdot O\cdot CO\cdot NHPh\end{matrix}$, which is deposited in yellow, transparent needles melting at 69—70° with decomposition. On recrystallisation from alcohol, colourless needles are obtained which melt at 77° with evolution of gas, and are converted into carbanilidothiophenantialdoxime (see below) on further heating with alcohol.

Thiophenantialdoxime, $\begin{matrix}C_4SH_3\cdot C\cdot H\\ \|\\ HO\cdot N\end{matrix}$, is obtained as a slightly coloured, viscid liquid by treating thiophenaldehyde (1·9 grams) with a mixture of hydroxylamine hydrochloride (2 grams) and sodium hydroxide (4 grams) in aqueous solution, hydrogen sodium carbonate (9 grams) is then added, and the liquid extracted with ether; the same compound is also obtained by the action of soda on the carbanilido-derivative (see above); it is slowly changed, at ordinary temperatures, into the syn-modification, whilst with hydrogen chloride the change is immediate.

Carbanilidothiophenantialdoxime is obtained from the syn-isomeride

as already described, and also by the combination of its constituents; it crystallises in groups of colourless, slender needles melting at 144°. The molecular weight was determined by Raoult's method. The antialdoxime combines with aniline to form a compound which is deposited in long, colourless plates melting at 45—46°, and gives a violet coloration with calcium hypochlorite. With orthotolyl cyanate, both the anti- and syn-aldoximes yield *carborthotoluidothiophensynaldoxime*, $\begin{matrix}C_4SH_3\cdot C\cdot H\\ \|\\ N\cdot O\cdot CO\cdot NH\cdot C_6H_4Me\end{matrix}$, which is deposited from ether in small, yellow needles melting at 66° with decomposition; on treatment with soda, orthoditolylcarbamide, orthotoluidine, thiophensynaldoxime, and thiophenic acid are formed.

It thus appears that the benzene antialdoximes, in their behaviour towards tolyl cyanate, differ from those of furfuraldehyde and thiophenaldehyde.

Œnanthaldoxime.—Methylœnanthaldoxime, $C_6H_{13}\cdot CH<\begin{matrix}NMe\\ |\\ O\end{matrix}$, is prepared by the action of methyl iodide on the oxime, and is a viscid, yellow liquid readily soluble in ether, alcohol, or benzene, but more sparingly in water. On boiling with dilute sulphuric acid, œnanthaldehyde and β-methylhydroxylamine are formed, whilst, on heating with hydriodic acid, methylamine is obtained.

Benzylœnanthaldoxime, $C_6H_{13}\cdot CH<\begin{matrix}N\cdot CH_2Ph,\\ |\\ O\end{matrix}$ is prepared in a similar manner to the preceding compound, which it resembles in its reactions; it crystallises from benzene in colourless, lustrous plates melting at 83°. Œnanthaldoxime combines with phenyl cyanate to form a viscid, unstable compound.

By the action of œnanthaldehyde on hydroxylamine hydrochloride in alkaline solution, a yellow, viscid liquid is obtained which is probably the *antialdoxime;* it is soluble in ether, and does not crystallise even in presence of the synaldoxime, but on treatment with hydrogen chloride in ethereal solution and subsequent evaporation of the latter, the synaldoxime is deposited in crystals.

The cyanates employed by the authors were made by heating the corresponding urethane (in portions of 15 grams) with 2 parts of phosphoric anhydride; the distillate is fractionated once, and is then pure. The yield is 52—53 per cent. of the theoretical in the case of phenyl cyanate, and 67·3 per cent. in that of orthotolyl cyanate.

J. B. T.

Dipropargyl and Benzene. By J. W. Brühl (*Ber.*, **25**, 2638—2646).—Up to the present, the molecular heat of combustion of dipropargyl (854—883 Cal.) has not been accurately determined, but is certainly much greater than that of benzene (784—788 Cal.); this is in harmony with the chemical behaviour of the two substances which indicates that the intramolecular tension is greater in dipropargyl than in benzene. The author has already conjectured (Abstr., 1891, 630) that the differences between the molecular refractions and dispersions of these two hydrocarbons are in the opposite sense to the

differences between the heats of combustion; this is now shown to be the case. The dipropargyl employed was purified by distillation in a slow current of air in a vacuum at the ordinary temperature; a very slight resinous residue was left, and the hydrocarbon was obtained as a colourless liquid which turned yellow in a few hours. The molecular refraction of dipropargyl (25·74 for sodium light) is considerably less than that of benzene (26·13), and agrees remarkably well with the calculated value considering the great difficulty of preserving the hydrocarbon unchanged during the measurement. The presence of two acetylenic bonds in dipropargyl is thus clearly indicated, and the spectrometrical data are in complete accord with the chemical behaviour of the substance. W. J. P.

Action of Chlorine on Orthonitrotoluene in presence of Sulphur. By C. Haeussermann and C. Beck (*Ber.*, **25**, 2445—2446). —When orthonitrotoluene is added to half its weight of sulphur, heated to 130—140°, and chlorine passed in until the evolution of hydrogen chloride ceases, the fatty, and not the aromatic, part of the hydrocarbon is attacked, 30 per cent. of the latter being converted into orthonitrobenzyl chloride. C. F. B.

Derivatives of Metaxylene. By C. Ahrens (*Annalen*, **271**, 15—20).—*Diacetylnitroxylidine* [$Me_2 : NAc_2 : NO_2 = 1 : 3 : 4 : 6$] is obtained when nitroxylidine (m. p. 123°) is boiled for an hour with excess of acetic anhydride; it crystallises in colourless, well-defined plates, melts at 115°, and, on boiling with dilute alcohol, is converted into the monacetyl derivative (m. p. 161°) described by Grevingk (Abstr., 1885, 144).

Nitrometaxylenediazopiperidide, $NO_2{\cdot}C_6H_2Me_2{\cdot}N_2{\cdot}C_5NH_{10}$, crystallises from alcohol in golden needles, melts at 51—52°, and is decomposed by concentrated halogen acids yielding the corresponding halogen derivatives of nitrometaxylene.

Fluoronitrometaxylene, $C_6H_2Me_2F{\cdot}NO_2$, is a volatile oil; the corresponding *chloro*-derivative, $C_6H_2Me_2Cl{\cdot}NO_2$, crystallises in needles, melts at 42°, and is soluble in alcohol; the *bromo*-derivative, $C_6H_2Me_2Br{\cdot}NO_2$, is volatile with steam, and forms long needles which melt at 57°; the *iodo*-derivative, $C_6H_2Me_2I{\cdot}NO_2$, is a brownish-yellow, crystalline compound melting at 86°.

Cyanonitrometaxylene, $NO_2{\cdot}C_6H_2Me_2{\cdot}CN$, crystallises from alcohol in long needles, and melts at 108—109°.

Nitrometaxylylic acid, $NO_2{\cdot}C_6H_2Me_2{\cdot}COOH$, prepared by heating the cyanide with concentrated hydrochloric acid at 150°, crystallises from hot alcohol in long, lustrous needles, melts at 196—197°, and is only sparingly soluble in boiling water, but readily in hot alcohol; it is probably identical with the acid obtained by Schaper (*Zeit. f. Chem.*, 1867, 13) by the oxidation of nitropseudocumene. The *amide*, $NO_2{\cdot}C_6H_2Me_2{\cdot}CO{\cdot}NH_2$, is a crystalline compound melting at 183°. The *ethyl* salt, $NO_2{\cdot}C_6H_2Me_2{\cdot}COOEt$, crystallises from dilute alcohol in needles, and melts at 75—76°. F. S. K.

Bivalent Carbon. By J. U. Nef (*Annalen*, **270**, 267—335).—Although carbonic oxide is an unsaturated compound, it is, relatively, very inert; it does not combine with iodine, or with halogen acids at 200°; it absorbs chlorine only very slowly in diffused light, and even in direct sunlight it is only very slowly and incompletely acted on by bromine. If, in the place of the oxygen atom in carbonic oxide, some less negative group were introduced, a substance would be obtained which would doubtless possess greater chemical activity than carbonic oxide; such substances are, possibly, hydrogen cyanide and its salts, and the isocyanides or carbylamines.

Starting from this assumption, the author has studied the properties of some isocyanides; he claims to have proved that they contain bivalent carbon, and are represented by the general formula R·N:C; he is also of opinion that the constitution of hydrogen cyanide is very probably expressed by the formula H·N:C. The following are the grounds on which the existence of a bivalent carbon atom in the isocyanides is assumed:—The isocyanides combine with halogens and with halogen acids, even at −15°, with development of great heat, yielding products of the constitution $R·N:CX_2$ and $(R·N:CHX)_2,HX$ respectively. They are readily converted into thiocarbimides by sulphur at 130°, and into thiamides by hydrogen sulphide at 100°. They combine with carbonyl chloride at −15° yielding compounds of the general formula R·N:CCl·CO·CCl:N·R, and with acetic chloride at 100° they form imidochlorides of pyruvic acid of the general formula R·N:CClAc. They combine with primary amines at 180—220°, yielding formamidine derivatives of the constitution R·N:CH·NHR′. Orthotolyl isocyanide combines directly with benzoic chloride at 100° yielding the compound described below.

Phenyl isocyanide, PhN:C, prepared by treating aniline with chloroform and alcoholic potash, freed from aniline and diphenylformamidine by shaking its ethereal solution with dilute hydrochloric acid, and purified by distillation, is a colourless oil, which soon turns greenish-yellow on keeping. It boils at 64° under a pressure of 20 mm., at 71° under a pressure of 30 mm., and at 78° under a pressure of 40 mm., leaving a small quantity of a blue residue; the distillate is colourless, but soon turns blue, and then gradually darkens; after some time, deep purple-red needles are deposited, and, on long keeping, the whole is converted into a solid resin, which is probably a polymeride. Phenyl isocyanide is reduced by sodium and boiling amyl alcohol, being reconverted into methylaniline; when treated with glacial acetic acid at the ordinary temperature, it yields formanilide and acetic anhydride, together with considerable quantities of acetanilide. It reacts violently with anhydrous formic acid, even at 0°, yielding formanilide and carbonic oxide, the latter being probably generated by the decomposition of the formic anhydride which is doubtless produced as an intermediate product; with anhydrous oxalic acid at 0°, it yields formanilide, carbonic oxide, and carbonic anhydride, a reaction which seems to show that oxalic anhydride is also incapable of existence. When heated at 130° with an alcoholic solution of sodium ethoxide, it yields a large quantity of diphenylformamidine; it reacts with silver oxide and with mercuric oxide

with explosive violence, but, when diluted with ether and then warmed with mercuric oxide at 40—50°, it gives traces of phenyl cyanate, the oxide being reduced to metal.

Isocyanophenyl dichloride (*phenylimidocarbonyl chloride*), $NPh{:}CCl_2$, is formed when chlorine is passed into a well-cooled chloroform solution of phenyl isocyanide until the colour of the solution suddenly changes from blue to yellow. It is a colourless oil, boils at 209—210° (thermometer entirely in vapour), and has a very irritating action on the eyes. When heated with glacial acetic acid, it yields acetaniilide; with water, symmetrical diphenylcarbamide; with silver oxide, phenyl cyanate; with alcohol, phenylurethane; with aniline, α-triphenylguanidine hydrochloride. The isocyanophenyl dichloride, previously described by Sell and Zierold (*Ber.*, **7**, 1228), is a mixture of the compound described above with a chloro-derivative, $C_6H_4Cl{\cdot}N{:}CCl_2$.

Phenyl isocyanide combines with bromine (1 mol.) in cold chloroform solution, yielding a yellow, unstable oil, which cannot be distilled, but which has, doubtless, the constitution $NPh{:}CBr_2$; it also combines with iodine (1 mol.) in carbon bisulphide solution to form an oily product.

Mesoxanilide imidochloride (*phenylamidomesoxalic chloride*),

$$NPh{:}CCl{\cdot}CO{\cdot}CCl{:}NPh,$$

can be obtained by treating phenyl isocyanide with carbonyl chloride at −20°, and then allowing the temperature of the mixture to rise slowly; it is a thick, yellow, hygroscopic oil, boils at 145—152° under a pressure of 15—20 mm., with slight decomposition, and is decomposed by cold 10 per cent. soda, yielding a considerable quantity of phenyl isocyanide.

Mesoxanilide alcoholate, $NPh{:}C(OH){\cdot}C(OH)(OEt){\cdot}C(OH){:}NPh$, is formed when the imidochloride is treated with water, and the solid hydrate obtained in this way recrystallised from boiling alcohol. It forms long, moss-like, colourless needles, begins to turn yellow at 100°, and melts at 145—151° with decomposition; it is readily soluble in dilute soda and in hot alcohol, but only very sparingly in cold alcohol and boiling water; it undergoes dissociation in boiling alcoholic or boiling benzene solution, combination taking place again on cooling. It combines with phenylhydrazine, forming a colourless substance of the constitution

$$NPh{:}C(OH){\cdot}C(N_2H_2Ph)(OEt){\cdot}C(OH){:}NPh;$$

this compound loses alcohol at 115°, being converted into mesoxanilidephenylhydrazone (see later).

Mesoxanilide, $NPh{:}C(OH){\cdot}CO{\cdot}C(OH){:}NPh$, prepared by heating the alcoholate or hydrate at 108—116° for about 16 hours, is a yellow powder, and combines readily with water and with alcohol to form the colourless hydrate and alcoholate respectively; it sinters at 163°, melts at 190°, and can be sublimed in small quantities. It combines with phenylhydrazine in dry benzene solution, yielding a compound of the constitution $NPh{:}C(OH){\cdot}C(N_2H_2Ph)(OH){\cdot}C(OH){:}NPh$, which, when heated at 100°, is converted into mesoxanilidephenylhydrazone.

Mesoxanilidephenylhydrazone, $NPh{:}C(OH){\cdot}C(N_2HPh){\cdot}C(OH){:}NPh$,

crystallises from glacial acetic acid in yellow plates, melts at 163° with decomposition, and is moderately easily soluble in glacial acetic acid acetone, and benzene, but only sparingly in alcohol and ether, and insoluble in alkalis; it does not combine with water or with alcohol.

Mesoxanilide hydrate, $NPh{:}C(OH)\cdot C(OH)_2\cdot C(OH){:}NPh$, separate from boiling water, in which it is only very sparingly soluble, in colourless needles, and behaves like the corresponding alcoholate when heated in a capillary tube; it is soluble in benzene and ethyl acetate, and also in warm dilute soda and sodium carbonate, from which it is precipitated unchanged by acids. It is a strong acid, and turns blue litmus red; when boiled with soda, it is decomposed into aniline and mesoxalic acid.

When ethyl oxanilate is hydrolysed with alcoholic potash, it yields an oxanilic acid melting at 210°, which is probably a polymeride of the known oxanilic acid; on treatment with phosphorus pentachloride, this supposed polymeride is converted into oxanilic chloride (m. p. 82·5°), which, when decomposed with water, yields the known oxanilic acid (m. p. 149°).

Pyruvic anilide imidochloride (*phenylimidopyruvic chloride*), $NPh{:}CClAc$, can be obtained by slowly and carefully heating a mixture of pure phenyl isocyanide and acetic chloride to about 100° on a water-bath; the product is freed from polymerides by dissolving it in ether. It is a yellow, hygroscopic oil, boils at 136° under a pressure of 30 mm., and is very unstable, gradually decomposing into acetic chloride and polymeric phenyl isocyanide, on keeping; when treated with alcohol, it is converted into diphenylformamidine hydrochloride, and, when poured into dilute acid, it is decomposed into hydrogen chloride, acetic acid, and phenyl isocyanide.

Pyruvic anilide, $NPh{:}CAc\cdot OH$, is produced when the preceding compound is treated with water; it crystallises in long, colourless needles, melts at 104°, and is readily soluble in hot alcohol and chloroform, but only moderately easily in ether, and almost insoluble in cold water; it is only slowly acted on by boiling dilute hydrochloric acid and dilute sulphuric acid, but is immediately decomposed by cold dilute soda, being converted into a colourless, flocculent substance which melts at 196°, and is probably a polymeride. When treated with phenylhydrazine in cold ethereal solution, it yields a colourless additive compound of the constitution

$$NPh{:}C(OH)\cdot CMe(OH)\cdot N_2H_2Ph;$$

this melts at 101—105° with liberation of water, and, when warmed with soda, it is decomposed into aniline and pyruvic acid. The *hydrazone*, $NPh{:}C(OH)\cdot CMe{:}N_2HPh$, prepared by heating the additive product at 78°, or by boiling it with alcohol or glacial acetic acid, crystallises in colourless needles, melts at 176°, and dissolves freely in hot benzene, alcohol, and glacial acetic acid, but is insoluble in alkalis and dilute acids.

Phenylimidoformic chloride hydrochloride, $2NPh{:}CHCl,HCl$, can be obtained by shaking an ethereal solution of phenyl isocyanide, cooled to −15°, with anhydrous hydrogen chloride. It is a colourless, very hygroscopic, unstable powder, and is decomposed by water and

alcohol with considerable development of heat; it is soluble in chloroform, but insoluble in ether and light petroleum. When treated with cold soda, or with water, it yields formanilide, diphenylformamidine, aniline, and formic acid.

The compound formed by the combination of anhydrous hydrogen cyanide with anhydrous hydrogen iodide, and described by Gautier (*Bull. Soc. Chim.* [4], **17**, 143), is very unstable, and could not be analysed; attempts to prepare imidoformic chloride and phenylimidoformic chloride were unsuccessful.

Orthotolyl isocyanide, $C_6H_4Me{\cdot}N{:}C$, prepared from orthotoluidine, as described in the case of the corresponding phenyl derivative, is a colourless oil, boils at 75° under a pressure of 16 mm., at 101° under a pressure of 55 mm., and at 183—184° with slight decomposition under a pressure of 753 mm.; it is much more stable than phenyl isocyanide, and does not readily undergo polymerisation, but when heated at 235—245° for three hours it is completely converted into orthotolyl cyanide. It is decomposed by formic acid, yielding carbonic oxide and formorthotoluidide, and with acetic acid it gives acetic anhydride, formorthotoluidide, and acetorthotoluidide; its behaviour with oxalic acid is similar to that of phenyl isocyanide, and, when heated with benzoic acid, it yields benzoylorthotoluidide as principal product. It is decomposed by orthotoluidine at 190—220° with formation of di-orthotolylformamidine (m. p. 151°); when heated with aniline at 190—220°, it yields a mixture of products, from which diphenylformamidine alone could be isolated. It combines with carbon bisulphide at 130°, yielding orthotolylthiocarbimide; when heated with an alcoholic solution of hydrogen sulphide at 100°, it gives thioformorthotoluidine (m. p. 100—101°).

Isocyanorthotolyl dichloride (tolylimidocarbonyl chloride),

$$C_6H_4Me{\cdot}N{:}CCl_2,$$

is formed when dry chlorine is passed into a well-cooled chloroform solution of orthotolyl isocyanide; it is a colourless oil, and boils at 214—215° (compare Lachmann, *Ber.*, **12**, 1349); when treated with orthotoluidine, it is converted into tri-orthotolylguanidine hydrochloride.

Mesoxatoluidide hydrate,

$$C_6H_4Me{\cdot}N{:}C(OH){\cdot}C(OH)_2{\cdot}C(OH){:}N{\cdot}C_6H_4Me,$$

can be obtained by treating orthotolyl isocyanide with carbonyl chloride in the cold, and decomposing the product with water; it crystallises from hot water, in which it is only very sparingly soluble, in colourless needles, turns yellow at 100°, and melts at 127—131° with decomposition. It turns blue litmus red, is soluble in dilute sodium carbonate, and is decomposed into its constituents by boiling anhydrous benzene, combination taking place again, to a certain extent, on cooling the solution.

Pyruvic orthotoluidide, $C_6H_4Me{\cdot}N{:}CAc{\cdot}OH$, seems to be produced, together with formorthotoluidide, when orthotolyl isocyanide is warmed with acetic chloride for five minutes on the water-bath, and the unstable imidochloride obtained in this way slowly poured into a

large volume of water; the aqueous solution is extracted with ether, the extract shaken with soda, the alkaline liquid acidified, extracted with ether, and the ethereal solution evaporated. The compound obtained in this way crystallises in hexagonal plates, melts at 62°, and is very readily soluble in water; it is probably a *hydrate* of the constitution $C_6H_4Me{\cdot}N{:}C(OH){\cdot}CMe(OH)_2$, as, when treated with calcium chloride in ethereal solution, it is transformed into a crystalline compound, melting at 177°, which is probably a polymeride; the latter is insoluble in ether and water, but readily soluble in hot alcohol and in dilute soda, from which it is reprecipitated by acids.

Benzoylformorthotoluidide, $C_6H_4Me{\cdot}N{:}CBz{\cdot}OH$, prepared by heating orthotolyl isocyanide with benzoic chloride on the water-bath, and decomposing the product with water, crystallises from ether in colourless needles, melts at 108°, and is readily soluble in hot ether and alcohol, but almost insoluble in boiling water. It dissolves in warm soda, being reprecipitated on acidifying the solution, but, when boiled with excess of potash, it is decomposed with formation of orthotoluidine; it is very stable towards concentrated hydrochloric acid and sulphuric acid. When its warm solution is treated with phenylhydrazine and then cooled, the colourless *hydrate* of the hydrazone is precipitated; this compound has doubtless the constitution

$$C_6H_4Me{\cdot}C(OH){\cdot}CPh(OH){\cdot}N_2H_2Ph,$$

and when its solutions are heated it is quickly converted into a yellow *hydrazone;* it is not decomposed by cold soda, but when warmed with sodium ethoxide in alcoholic solution it is converted into the hydrazone of benzoylformic acid.

Paratolyl isocyanide, $C_6H_4Me{\cdot}N{:}C$, is a colourless oil, boiling at 99° with slight decomposition under a pressure of 36 mm.; it undergoes change only slowly on keeping.

Isocyanoparatolyl dichloride, $C_6H_4Me{\cdot}N{:}CCl_2$, is a colourless oil with an irritating odour, and boils at 225—226° (uncorr.); when treated with paratoluidine, it is converted into triparatolylguanidine hydrochloride.

The above experiments having shown that phenylhydrazine combines with certain compounds containing a carbonyl group to form additive products, which are converted into hydrazones by the loss of 1 mol. H_2O, the author, arguing from analogy, assumes that when hydroxylamine combines with ketones, additive compounds are first formed; he supposes that in the production of benziledioxime, for example, there is formed an intermediate product of the constitution $OH{\cdot}NH{\cdot}CPh(OH){\cdot}CPh(OH){\cdot}NH{\cdot}OH$, which, by loss of 2 mols. H_2O, is converted into the dioxime; this last stage of the reaction can take place in three different ways, yielding, in each case, a dioxime which is chemically isomeric with the other two. Since it may be assumed that similar intermediate products are formed in other cases, it is quite possible that the supposed stereochemical isomerism of the oximes is, in reality, a matter of true chemical isomerism, especially as, in the author's opinion, not a single fact to the contrary has yet been established.

The rest of the paper consists of a discussion of the constitution of

hydrogen cyanide and of short replies to v. Pechmann (this vol., p. 431) and to Brühl (this vol., p. 583). F. S. K.

Homocatechol and two Nitrohomocatechols. By H. Cousin (*Compt. rend.*, **115**, 234—236).—The product of the action of hydrogen iodide on creosol at 180° is fractionated, and the portion boiling between 230° and 265° is repeatedly treated with boiling water, the solution being filtered after cooling and evaporated on a water-bath. The syrupy liquid thus obtained is distilled under reduced pressure. The greater part boils at 210—215° under a pressure of 190 mm., and forms a colourless, viscous liquid, which solidifies to a crystalline mass melting at 49—50°. It contains a small quantity of catechol.

Homocatechol (11 grams) is dissolved in ether (500 c.c.), mixed gradually with fuming nitric acid (4 c.c.), and, after 24 hours, agitated with a small quantity of water. The ethereal layer is distilled, and the residue is mixed with water and again distilled. The condensed water is yellow, and contains oily drops; it is heated until these drops dissolve, and then allowed to cool, when *nitrohomocatechol*, $C_7H_7NO_4$, separates in golden-yellow lamellæ, which melt at 79—80°, begin to decompose at about 180°, are coloured deep red by alkalis, and dissolve slightly in cold water, but are more soluble in hot water, alcohol, and ether.

Homocatechol (5 grams) is dissolved in water (150 c.c.), mixed with a solution of sodium nitrite (18·5 grams), and dilute hydrochloric acid added gradually until there is an abundant evolution of nitrogen oxides. The deep-red mixture is extracted with ether, which is separated and distilled, and the brown, crystalline residue is dried over sulphuric acid; it is then crystallised from boiling benzene and finally from dilute alcohol. This compound is a *nitrohomocatechol*, $C_7H_7NO_4$, but is isomeric with the preceding compound. It forms small, sulphur-yellow needles, only slightly soluble in cold water, but soluble in hot water, alcohol, ether, or benzene; it melts at about 180° with incipient decomposition. When treated with excess of alkali, it gives a beautiful, purple coloration. If, however, potassium hydroxide or ammonia is added to a hot solution until the purple coloration just begins to be produced, the liquid, when cooled, deposits orange-yellow needles of the monobasic alkali salts, which are easily purified by recrystallisation from water. The *potassium* salt has the composition $C_7H_6KNO_4 + H_2O$. C. H. B.

Condensation of Unsaturated Hydrocarbons with Phenols. By W. Koenigs and C. Mai (*Ber.*, **25**, 2649—2658).—One of the authors has already described the condensation of monatomic phenols with unsaturated hydrocarbons (Abstr., 1891, 571, and this vol., p. 446). The present paper deals with the behaviour of polyatomic phenols. Quinol, resorcinol, and catechol unite with 2 mols. of the unsaturated hydrocarbons, and well-crystallised diamyl derivatives were obtained. Pyrogallol yields a diamyl derivative, but a triamyl derivative could not be obtained.

Diamylquinol, $C_6H_2(C_5H_{11})_2(OH)_2$, is obtained by adding sulphuric acid (50 c.c.), with cooling, to a solution of quinol (25 grams) in

acetic acid (250 grams), and then gradually adding isoamylene (50 grams, 2·5 mols.) to the cold mixture. After 24 hours, the crystalline product is collected, washed with acetic acid, dissolved in ether, and the ethereal solution shaken with soda, dried over potash, evaporated to dryness, and the crystalline mass thus obtained is recrystallised from benzene. It forms colourless, compact, tetragonal pyramids, melts at 185°, is easily soluble in alcohol, ether, and chloroform, less so in cold benzene and acetic acid, very sparingly in light petroleum, almost insoluble in water, and in soda, ammonia, and the fixed alkalis. The concentrated alcoholic solution turns yellowish-red on the addition of potassium or sodium hydroxide, but, on adding water, unaltered diamylquinol is precipitated. When warmed in alkaline alcoholic solution, it yields diamylquinone. Phenylhydrazine and hydroxylamine are without action on diamylquinol. Ferric chloride, ordinary and fuming nitric acid, and bromine in carbon bisulphide all convert it into the corresponding quinone. When warmed with concentrated sulphuric acid, it is decomposed. It cannot be sublimed without decomposition, is not volatile with steam, and is very stable towards light and air.

Diacetyldiamylquinol, $C_6H_2(C_5H_{11})_2(OAc)_2$, is obtained by boiling the preceding compound with acetic anhydride. It crystallises from alcohol in beautiful, four-sided tablets, melts at 116°, is easily soluble in the ordinary organic solvents, and insoluble in water. When boiled with dilute alcoholic sulphuric acid, it yields diamylquinol; with alcoholic potash, it yields diamylquinone.

Diamylquinol phenylcarbamate, $(NHPh\cdot COO)_2C_6H_2(C_5H_{11})_2$, is obtained by warming diamylquinol with phenyl isocyanate. It is insoluble in most solvents, dissolves sparingly in acetone and acetic acid, separates as a crystalline powder, and melts at 248°.

Quinol diisoamyl ether, $C_6H_4(OC_5H_{11})_2$, is obtained by gradually adding a solution of potassium hydroxide (3·1 grams) in alcohol (15 c.c.) to a warm mixture of quinol (3 grams) and isoamyl iodide (11 grams). It crystallises in silky, colourless needles, melts at 65°, is volatile with steam, and is very easily soluble in organic solvents, with the exception of cold alcohol, in which it is somewhat sparingly soluble.

Neither the diisoamyl ether nor the diacetate of quinol yields condensation products with amylene.

Diamylquinone, $C_6H_4O_2(C_5H_{11})_2$, is obtained by boiling a mixture of diamylquinol (5 grams), alcohol (50 grams), and dry ferric chloride (15 grams) in a reflux apparatus for one hour. It crystallises from alcohol in long, bright yellow needles, melts at 140°, sublimes in beautiful, slender, pale yellow needles, is easily volatile with steam, and is easily soluble in ether, benzene, chloroform, and acetone, somewhat sparingly so in cold alcohol and acetic acid, sparingly in light petroleum, and almost insoluble in water. It is not altered by treatment with sulphurous acid, but when boiled with zinc-dust and acetic acid, it is reconverted into diamylquinol. It is not attacked by alkalis, calcium chloride, aniline, phenylhydrazine, hydrogen bromide, hydroxylamine, acetic anhydride, or phenyl isocyanate.

Diamylresorcinol, $C_6H_2(C_5H_{11})_2(OH)_2$, is obtained in a similar way to diamylquinol. It crystallises from light petroleum in slender,

colourless needles, melts at 89°, is extremely soluble in all organic solvents, and is insoluble in water, soda, and ammonia. It dissolves easily in potassium, sodium, and barium hydroxides, and is precipitated from the solution unchanged by the addition of acids. It is easily volatile with steam. When boiled in alcoholic solution with methyl iodide and potassium hydroxide, it yields a dimethyl ether which melts at 64°. The *diacetyl derivative* melts at 89°.

Diamylcatechol is obtained by allowing a mixture of catechol, acetic acid, sulphuric acid, and amylene to remain five days. The oily product is freed from polyamylenes by distillation in a vacuum at 100°, and the residue distilled with steam, dried on porous plates in a vacuum, and crystallised from light petroleum. It crystallises in aggregates of colourless needles, melts at 60°, is very easily soluble in organic solvents, and insoluble in alkalis. When the alcoholic solution is treated with a few drops of concentrated potassium hydroxide solution, it assumes a beautiful, blue colour, which changes to dirty green on the addition of water, and an oil is precipitated, which turns to a dark-green resin when warmed. With ferric chloride, the alcoholic solution gives a green coloration, and, with lead acetate, a white, gelatinous precipitate, which quickly turns green when dried. The authors were unable to determine if diamylcatechol contains two hydroxyl groups, owing to lack of material.

Diamylpyrogallol, $C_6H(C_5H_{11})_2(OH)_3$, is obtained when a mixture of pyrogallol, amylene, acetic acid, and sulphuric acid is left for 5 to 6 days. It crystallises from light petroleum in long, colourless needles which turn red on exposure to air, melts at 90°, is not volatile with steam, is very easily soluble in organic solvents, insoluble in water, sodium carbonate, and ammonia, and dissolves easily in sodium and potassium hydroxides, yielding a solution which at once turns violet. With ferric chloride, the alcoholic solution gives first a green and then an intense violet coloration. The *triacetate* crystallises from alcohol in colourless, lustrous needles, and melts at 145°.

The authors also describe experiments with tetrahydronaphthylphenol and metacresolphenylethane.

Tetrahydronaphthylphenol, $C_{10}H_{11}\cdot C_6H_4\cdot OH$, is obtained by the condensation of dihydronaphthalene with phenol. When mixed with pumice and heated to dull redness in a current of carbonic anhydride, it is partially resolved into naphthalene and phenol, and the remainder distils unchanged. Naphthylphenol cannot be obtained from it by distillation with zinc-dust or with lead oxide.

Tetrahydronaphthylanisoïl, $C_{10}H_{11}\cdot C_6H_4\cdot OMe$, is obtained by boiling tetrahydronaphthylphenol with potash, methyl alcohol, and methyl iodide for four hours in a reflux apparatus. It crystallises from alcohol in beautiful, long, silky needles, melts at 71°, and is very easily soluble in ether, chloroform, benzene, and carbon bisulphide, more sparingly in cold alcohol, and almost insoluble in water. When treated with excess of bromine, it yields a mixture of di- and tri-brominated derivatives. The authors were unable to obtain naphthylanisoïl from it.

Kraemer and Spilker (Abstr., 1891, 206) have stated that the hydrocarbons obtained by the condensation of cinnamene with homo-

logues of benzene, by means of sulphuric acid, are converted into anthracene derivatives when heated at a dull red heat. The authors have examined the behaviour of metacresolphenylethane, and find that, when heated with zinc-dust, it is decomposed with formation of metacresol. When heated alone, a fluorescent compound was obtained, which dissolves in alkali with a yellow coloration, and is, perhaps, hydroxyanthracene; but the yield was so small that satisfactory results could not be obtained.

The bye-products formed in the preparation of metacresolphenylethane were found to contain unaltered cresol, and the liquid dicinnamene, $C_{16}H_{16}$, which boils at 310°. The latter is also obtained in large quantities by allowing a solution of cinnamene in pure sulphuric acid (1 vol.) and acetic acid (9 vols.) to remain for a time.

E. C. R.

Constitution of Pyrogallol. By De Forcrand (*Compt. rend.*, **115**, 284—286).—The heat of neutralisation of pyrogallol by dilute soda as measured by Berthelot and Werner, namely, +6·40, +6·38, and +1·02 Cal., for the three successive hydroxyls, seems to indicate that the third hydroxyl occupies the ortho-position relatively to the others, since the corresponding values for catechol are +6·26 and +1·40 Cal., whilst those for resorcinol are +8·22 and +7·36, and for quinol +8·00 and +6·36. The mean value for pyrogallol (4·60), moreover, is less than that for phloroglucol (+6·09), just as the mean value for catechol (+3·83) is less than that for its isomerides (+7·79). In drawing conclusions, however, from successive values obtained with dilute solutions, it is necessary to be cautious on account of the very considerable influence of the heat of dissolution. Catechol, for instance, which is apparently the weakest of the three dihydroxybenzenes, is found to be the strongest when the heat of dissolution is taken into account (see this vol., p. 1184).

To clear up the matter, the authors have redetermined the heat of neutralisation of the successive hydroxyls of pyrogallol, calculated for the solid state. The total amount is +116·09 Cal., giving a mean value of +38·70 for each hydroxyl. The successive values are approximately +41·34, +39·09, and +35·66 Cal. On comparing the mean value with those for resorcinol, +38·60, catechol, +39·02, and quinol, +37·36, it would seem that the constitution 1 : 3 : 5, analogous to that of resorcinol, is the more probable, were it not that the properly calculated successive values (+38·70 and +38·50 for resorcinol), which have a far greater indicative power than the mean values, show the essential constitutional difference between the two substances, namely, the ability of pyrogallol and the inability of resorcinol to form intermediate molecular combinations in the course of neutralisation. The asymmetrical constitution, necessitating the para-position for the extreme hydroxyls, is seen to be impossible when the mean value for those groups (+38·50) is compared with those for quinol, and for the single hydroxyl of phenol (+39·10), and this value, moreover, is so near that for resorcinol as to point with certainty to the meta-position for the extreme groups. The third group, notwithstanding its ortho-position relatively to the others, bears practically the same value as the single hydroxyl of

phenol, probably because it has to be dislodged from a molecular combination before it can be neutralised, and thus acts as if it were independent of them. Jn. W.

Aromatic Sugars. By E. Fischer and A. J. Stewart (*Ber.*, **25**, 2555—2563).—*Phenyldibromhydroxybutyronitrile*,

$$CHPhPr{\cdot}CHBr{\cdot}CH(OH){\cdot}CN,$$

is prepared by dissolving cinnamaldehydecyanhydrin (100 grams) in chloroform (500 grams), and adding bromine (100 grams); the nitrile is precipitated on the addition of light petroleum, and crystallises from chloroform, dilute alcohol, or light petroleum, in small, colourless needles which darken at 130°, and melt at 140° with evolution of gas. The yield is quantitative.

On heating the nitrile with 20 parts of hydrochloric acid (20 per cent.) for two hours in a reflux apparatus, *phenylbromodihydroxybutyrolactone*, $CHPh<^{CHBr}_{O\cdot CO}>CH{\cdot}OH$, is formed, and crystallises from water in colourless needles which melt at 137° (uncorr.) without decomposition; it is sparingly soluble in ether, chloroform, and light petroleum, but readily so in alcohol. The aqueous solution is neutral. The yield is 15 per cent. of the theoretical.

Phenyltrihydroxybutyric acid is obtained by the action of barium hydroxide on the bromolactone in molecular proportion; after the removal of the barium and hydrobromic acid, and evaporation of the aqueous solution, the *lactone* is deposited in slender, colourless needles which melt at 115—117°. The *silver salt* of the acid crystallises from water in lustrous prisms or plates; the *sodium salt* is crystalline and soluble in alcohol. The *phenylhydrazone* is deposited from water in small, colourless prisms or plates which melt at 167°, with previous softening at 160°, and give a rose coloration on the addition of sulphuric acid and ferric chloride.

Phenyltetrose, $OH{\cdot}CHPh{\cdot}CH(OH){\cdot}CH(OH){\cdot}COH$, is prepared by the reduction of the lactone (5 grams) with 2·5 per cent. sodium amalgam (100 grams) in dilute alcoholic solution; the liquid is well cooled, and maintained acid by the frequent addition of sulphuric acid; the operation lasts $\frac{3}{4}$ hour; the solution is separated from the mercury, treated with soda in order to remove any unaltered lactone, neutralised with sulphuric acid, and evaporated to dryness in a vacuum; the residue is extracted with absolute alcohol, the solution treated with ether, and again evaporated to dryness; this residue is now extracted with ether, and after the removal of the latter, the tetrose remains as a colourless syrup which is readily soluble in water, alcohol, and ether, and reduces alkaline copper solutions on boiling. The *phenylhydrazone* crystallises from water in small, slender, lustrous plates, melting at 154°; it is sparingly soluble in ether and benzene, but more readily in alcohol. With concentrated sulphuric acid, a brown coloration is produced; with concentrated hydrochloric acid, the tetrose is regenerated.

On treating phenylhydroxycrotonic acid with bromine in chloroform solution, *phenylbromhydroxycrotonic acid*, $C_{10}H_9BrO_3$, is formed,

and is deposited from ether, on the addition of light petroleum, in colourless crystals, melting at 95—100°; the yield is 90 per cent. of the theoretical. By the action of soda at ordinary temperatures on the preceding compound, a *phenylketohydroxybutyric acid*, $CH_2Ph{\cdot}CO{\cdot}CH(OH){\cdot}COOH$ or $CH_2Bz{\cdot}CH(OH){\cdot}COOH$, is formed, which crystallises from water, or from ether on the addition of light petroleum, and melts at 118° (uncorr.). This acid reduces alkaline copper and silver solutions at the ordinary temperature, and becomes yellow on heating with alkalis. With phenylhydrazine, a yellow, amorphous, insoluble compound is formed. The *oxime* is deposited from water in hard, colourless, well developed crystals, which melt at 125° (uncorr.).

Phenylisodihydroxybutyric acid is prepared by the reduction of the ketonic acid with sodium amalgam; it is a colourless, viscid liquid, isomeric with Biedermann's phenyldihydroxybutyric acid. The *silver salt* is colourless and crystalline; the *phenylhydrazone* crystallises from water in small, colourless needles which melt at 161—162°. The yield is 30 per cent. of the acid employed. J. B. T.

Mercurioanilido-compounds. By L. Pesci (*Gazzetta*, **22**, 373—384).—A molecular compound of mercuriophenylamine and aniline is prepared by slowly adding 6 per cent. mercuric chloride solution (50 c.c.) to a mixture of a saturated aqueous solution (500 grams) of aniline, 30 per cent. aqueous soda (20 c.c.), and sufficient water to render the liquid clear. More soda (60 c.c.) and mercuric chloride (150 c.c.) are then cautiously added, and the white precipitate which separates collected, and washed with dilute aniline solution until the filtrate no longer contains chlorine. The product after drying over sulphuric acid has the composition $4NHgPh,5NH_2Ph$, and consists of microscopic, transparent octahedra, which have a caustic taste and a strongly alkaline reaction; when crystallised from water containing aniline (2 per cent.) and caustic potash (1 per cent.) at 80°, beautiful four-sided tables are obtained of the composition $6NPhHg,7NH_2Ph$; on crystallisation from potash (15 per cent.), however, it is deposited in splendid hexagonal tables, having the composition $NPhHg,NH_2Ph$. These three compounds are similar in properties, and are converted into a brown substance by the ordinary solvents. *Mercuriophenylamine*, NPhHg, is prepared by the action of dilute alkalis on the acetate suspended in water; it separates in colourless laminæ of a nacreous lustre. It has a strongly alkaline reaction and caustic taste, is sparingly soluble in water, insoluble in alcohol and ether, and on heating decomposes without melting. Its salts are obtained by the action of dilute acids on the preceding molecular compounds; they are decomposed by hydrogen sulphide with formation of mercuric sulphide. The *acetate*, $NPhHg,Ac{\cdot}OH$, forms brilliant, highly refractive, colourless crystals, which are very soluble in acetic acid, but insoluble in water, alcohol, and ether. The *nitrate* forms colourless, microscopic pyramids, which are soluble in potash and mineral acids, but insoluble in water. *Hydrogen mercuriophenylamine sulphate*, $NPhHg,H_2SO_4$, is obtained in colourless, microscopic needles, in-

soluble in water and alcohol, soluble in aqueous potash and mineral acids; it has an acid reaction, and decomposes at about 150° without melting. The *hydriodide* is obtained as a flocculent, yellow precipitate by the action of potassium iodide solution on the acetate; it is practically insoluble in water, alcohol, acids, and alkalis. The *hydrobromide* and hydrochloride (compare Förster, *Annalen*, **175**, 25) are amorphous, yellow powders, insoluble in water and mineral acids, and partially soluble in alkalis. The hydrochloride readily dissolves in a boiling alcoholic solution of aniline hydrochloride; on cooling, thin, colourless needles, having the composition $NPhHg,HCl,NH_2Ph,HCl$, separate. This substance has been prepared by Gerhardt (*Trait. de Chem. Org.*, iii, 86) and by H. Schiff (*Compt. rend.*, **56**); it decomposes at 150°, and its solution in boiling water, on cooling, deposits thin needles of a substance not yet studied.

W. J. P.

Additive Products of Hydrogen Iodide and Nitriles. By H. Biltz (*Ber.*, **25**, 2533—2545).—Benzonitrile combines very readily with concentrated hydriodic acid, forming a crystalline fairly stable additive product, having the composition $C_6H_5CN,2HI$, which may be preserved for months when anhydrous, but is decomposed by moisture. It forms lemon-yellow crystals, melts with decomposition at 135—140°, and on distillation splits up into its components, which partially reunite in the receiver. Most solvents also bring about the same change, but when heated with phenol, it yields ammonium iodide, a little phenyl benzoate, benzamide, and a colouring matter, which proved to be identical with benzaurine (Abstr., 1880, 239). The formation of the latter may be readily explained if the additive product is diiodobenzylamine, $C_6H_5{\cdot}CI_2{\cdot}NH_2$, the reaction taking place as follows:—

$$NH_2{\cdot}CPhI_2 + 2C_6H_5{\cdot}OH = OH{\cdot}C_6H_4{\cdot}CPh\begin{matrix}C_6H_4\\ O\end{matrix} + NH_4I + HI.$$

The compound therefore corresponds with the chloride,

$$C_6H_5{\cdot}CCl_2{\cdot}NH_2,$$

obtained by Wallach from phosphorus pentachloride and benzamide, but, unlike the latter, it is not converted into benzamide by the action of water.

The formation of similar additive compounds with hydrogen iodide takes place with a large number of both aliphatic and aromatic nitriles; in the former series, the iodides of acetamide, propionamide, and succinamide have been prepared from the corresponding nitriles, and all resemble the benzonitrile derivative in their general properties, but in addition yield by the action of water, a certain quantity of the amide and corresponding acid. Ortho-, meta-, and para-tolunitrile, ortho-, meta-, and para-nitrobenzonitrile, benzyl cyanide, terephthalonitrile, α- and β-naphthonitrile, and cinnamonitrile all yield dihydriodo-derivatives, whilst triphenylacetonitrile and mandelic nitrile are not acted on by hydriodic acid. All the compounds have a yellow to brown or red colour, and melt with de-

composition between 100° and 140°; none of the aromatic compounds yield the amide or corresponding acid on treatment with water.

H. G. C.

Condensation Products with Formaldehyde. By G. Pulvermacher (*Ber.*, **25**, 2762—2765).—Continuing his former work (this vol., p. 579), the author has investigated the condensation products obtained by the action of formaldehyde on the three nitranilines.

Methylenedimetanitraniline, $CH_2(NH\cdot C_6H_4\cdot NO_2)_2$, was obtained by adding an excess of a 40 per cent. solution of formaldehyde to an almost boiling solution of metanitraniline. It crystallises in orange-yellow needles insoluble in water, ether, benzene, and chloroform, sparingly soluble in alcohol, and melts at 213°. It is strongly basic in character. The *picrate* forms yellow needles melting at 120°; the *aurochloride* easily soluble, light yellow rhombs; the *platinochloride* sparingly soluble golden-yellow rods. *Methylenediparanitraniline* crystallises in fine, lemon-yellow needles melting at 232°. It is insoluble in water and ether, very sparingly soluble in alcohol. It is much less basic in character than the meta-compound, and no definite salts were obtained. *Methylenediorthonitraniline* is much less readily formed than its two isomerides. It crystallises in yellow needles, is sparingly soluble in alcohol, soluble in ether, and insoluble in water, and melts at 195°. The *picrate* and *aurochloride* are crystalline, the *platinochloride* amorphous. Even long continued boiling with hydrochloric acid caused no decomposition of the ortho-compound, whilst the meta- and para-compounds were slowly decomposed.

No reaction could be brought about between formaldehyde and picramide.

L. T. T.

Derivatives of Paradianilidobenzene. By O. Brunck (*Ber.*, **25**, 2715—2722).—It having been shown by O. Fischer and Hepp (Abstr., 1890, 911) that trianilidonaphthalene is readily converted into rosinduline on oxidation, the object of the present work was to ascertain whether, on oxidising amidoparadianilidobenzene [$NH_2 : (NHPh)_2 = 1:2:5$], an induline of the benzene series is formed. The author did not even succeed, however, in preparing the amido-derivative. Calm's paradianilidobenzene (Abstr., 1884, 591) melts at 146° (compare O. Fischer and Wacker, Abstr., 1888, 1286). The diacetyl derivative (Calm, *loc. cit.*), when heated on the water-bath with nitric acid of sp. gr. 1·4, gives a nitro-compound, $NO_2\cdot C_6H_3(NPhAc)_2$, which crystallises from alcohol in pale yellow needles, and melts at 160°. The nitro-compound, when boiled with alcoholic potash, gives a violet compound which may be an azo-derivative; on reduction with tin and hydrochloric acid, it yields a substance having phenolic properties, and this, if heated at 130° with 20 per cent. hydrochloric acid, gives aniline and a carbonaceous residue smelling distinctly of quinone, so that it is perhaps a quinoneoxime. Brandrowsky's diphenylparazophenylene (quinonedianil) is obtained by heating either paradianilidobenzene or its diacetyl derivative with alcoholic potash. The above-mentioned nitrodiacetylparadianilidobenzene, when boiled with alcoholic sulphuric acid, yields a compound which,

when heated with alcoholic ammonium sulphide, gives an *anhydro-base*, $NH^{4}Ph\cdot C_6H_3<\overset{1}{\underset{2}{NPh}}>CMe$, melting at 162—164°; if, however, the nitro-compound is first reduced, a *basic* substance, $C_{22}H_{19}N_3O$, melting at 180° is produced, which gives the last-mentioned anhydro-base on hydrolysis with alcoholic sulphuric acid.

Diformylparadianilidobenzene, $C_{20}H_{16}N_2O_2$, prepared by boiling paradianilidobenzene with formic acid of sp. gr. 1·2 (10 parts), crystallises from alcohol in white needles, and melts at 168°; when nitrated under the same conditions as the diacetyl derivative (see above), a *dinitro*-derivative melting at 215° is obtained. Calm's dibenzoylparadianilidobenzene (*loc. cit.*) yields a trinitro-derivative melting at 248°. A. R. L.

Condensation Products of the Amidophenols. By E. Haegele (*Ber.*, **25**, 2753—2756).—The author finds that the amidophenols, and especiallly paramidophenol, readily form condensation products with aldehydes and, with rather more difficulty, with ketones. The preparation is similar to that for hydrazones, a dilute acetic solution of the amidophenol being shaken with the aldehyde. Heat is developed, and the condensation product crystallises out. With ortho-amidophenol, the reaction requires the aid of heat.

Benzylideneparamidophenol, $CHPh{:}N\cdot C_6H_4\cdot OH$, from benzaldehyde and paramidophenol, crystallises in large scales easily soluble in alcohol, but insoluble in water, and melts at 163°. *Hydroxybenzylidene-paramidophenol*, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot OH$, from salicylaldehyde, forms yellow or orange scales soluble in boiling water and alcohol, and melts at 135°. No phenanthridine derivative could be obtained. Dilute sulphuric acid splits the compound up into its components. *Methoxybenzylideneparamidophenol*, $OMe\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot OH$, from anisaldehyde, crystallises in yellow prisms melting at 188°. It is soluble in boiling water and in ether or benzene. *Cinnamylideneparamidophenol*, $CHPh{:}CH\cdot CH{:}N\cdot C_6H_4\cdot OH$, forms pale green needles, melts at 223°, and is soluble in ether, benzene, and glacial acetic acid, sparingly so in cold water or alcohol. The *dibromo*- additive product forms very dark red needles sparingly soluble in alcohol, insoluble in water, and melts at 287°.

Isopropyleneparamidophenol, $CMe_2{:}N\cdot C_6H_4\cdot OH$, from acetone, crystallises from water in colourless needles melting at 158°. No corresponding condensation product could be obtained from acetophenone.

Hydroxybenzylideneorthamidophenol crystallises in needles melting at 175°. It is sparingly soluble in boiling water and in benzene, more readily in alcohol and in ether. *Methoxybenzylideneorthamidophenol* crystallises from alcohol in yellowish-brown needles melting at 89°. *Cinnamylideneorthamidophenol* crystallises from boiling alcohol in glistening needles, and melts at 79°. It is easily soluble in alcohol and in ether. L. T. T.

Condensation Products of Furfuraldehyde with Bases. By G. de Chalmot (*Annalen*, **271**, 11—14).—A condensation product of

the constitution $C_4OH_3{\cdot}CH{:}NPh$ is formed when aniline is mixed with the molecular quantity of furfuraldehyde. It separates from ether in yellowish crystals, melts at 58°, and boils at 163—164° (uncorr.) under a pressure of 19 mm.; it rapidly turns yellow and then red on exposure to the air, and when heated with aniline hydrochloride, it yields an intensely reddish-violet compound.

The compound of the composition $C_{12}H_{11}NO$, prepared from orthotoluidine in like manner, forms almost colourless crystals, melts at 54—55°, and boils at 171—172° under a pressure of 19 mm.; it turns red on exposure to the air, is decomposed by boiling acids, and combines with aniline and with toluidine yielding red dyes. The condensation product of furfuraldehyde and paratoluidine melts at 43—44°, and resembles the compound just described.

Furfuraldehyde and benzylamine react readily, yielding an oil of the constitution $C_4OH_3{\cdot}CH{:}N{\cdot}CH_2Ph$; this substance boils at 155° under a pressure of 11 mm., and is decomposed by boiling water.

The condensation product of furfuraldehyde and piperidine boils at 157—158·5° under a pressure of 14 mm., and has the composition $C_{15}H_{24}N_2O$; its *hydrochloride*, $C_{15}H_{24}N_2O,2HCl$, is very hygroscopic, and is quickly decomposed by water. F. S. K.

Condensation Products of Furfuraldehyde with Aromatic Bases. By G. J. L. de Chalmot (*Amer. Chem. J.*, **14**, 310—314). Furfuraldehyde, aniline, and aniline hydrochloride yield a violet-red crystalline compound, $2C_6H_7N,C_5H_4O_2,HCl$, without elimination of water. Schiff represented the composition of this furfuraniline by the formula $C_4OH_3{\cdot}CH(C_6H_4{\cdot}NH_2,HCl){\cdot}C_6H_4{\cdot}NH_2,H_2O$, but was unable to prepare free furfurandiphenylmethane.

The author obtained only negative results on attempting to obtain the base, although with solutions free from water.

With the corresponding toluidine compound, it was found that on drying for 9 hours at 100—105°, water was lost; the dried substance was no longer crystalline, but behaved towards solvents just like the crystalline compound. It had the composition $C_{19}H_{20}N_2O,HCl$.

Among the products of decomposition obtained on heating to 200° were colourless crystals of an aromatic base.

The author concludes that the water present in the compound is not united to one of the amido-groups, but is simply water of crystallisation. He wishes to reserve the investigation of the reaction between the compound $C_6H_5N{:}C_5H_4O$ and dimethylaniline.

W. T.

Stereoisomerism of Carbodiphenylimide and Carbodiparatolylimide. By C. Schall and S. Paschkowetzky (*Ber.*, **25**, 2880—2895).—The authors have succeeded in resolving carbodiphenylimide and carbodiparatolylimide respectively into two modifications (compare Weith, this Journal, 1874, 480; Will. Abstr., 1881, 905; Will and Bielschowsky, *ibid.*, 1882, 1091) by distillation under diminished pressure. The results vary according to the pressure under which the distillation is conducted, also according to the length of time the compounds have been kept after their preparation. See-

ing that the two modifications have the same molecular weights. the authors suggest that they are stereoisomerides, and propose to represent them by the following general configurations $\begin{matrix} RN \\ \| \\ C \\ \| \\ NR \end{matrix}$ and $\begin{matrix} NR \\ \| \\ C. \\ \| \\ NR \end{matrix}$

The following may be cited from the experimental portion:— Carbodiphenylimide (freshly prepared) boils at 218° (30·8 mm.); the distillate solidifies and has a melting point of 136°. When the latter is carefully crystallised from anhydrous benzene, it melts at 158—160°; whilst an oily modification which could not be completely freed from the solvent was obtained from the benzene solution. The oily modification is converted into the solid one on triturating it with alcohol, and when the latter is heated at 110°, the oily modification is formed. The oily modification is converted into carbanilide by boiling it with alcoholic hydrochloric acid, but this reaction takes place much less readily with the solid modification.

Carbodiparatolylimide (freshly prepared) boils at 238° (35 mm.); the distillate subsequently solidifies, and has a melting point of about 60°. When the latter is allowed to remain for 20 hours with dry light petroleum, filtered from the undissolved portion, and the solution evaporated, a modification melting at 49—50° is obtained; whilst when the substance melting at 60° is crystallised from anhydrous ether, and subsequently extracted with boiling light petroleum, a modification melting at 148—149° is isolated. When either of these modifications is distilled under diminished pressure, it is partially converted into the other. Diparatolylcarbamide is formed when the modification of lower melting point is boiled with alcoholic hydrochloric acid, or when that of higher melting point is boiled with acetic acid. A. R. L.

Constitution of Nitrosoazo-compounds. By C. Willgerodt (*Ber.*, **25**, 2661—2664).—Phenylazimidobenzene, dinitrosoazobenzene, and the two nitrodinitrosoazobenzenes, when boiled with a mixture of equal parts of fuming nitric and sulphuric acids for one hour, yield the same compound, namely tetranitrophenylazimidobenzene,

$$C_6H_3(NO_2)_2\cdot N<\begin{matrix} N \\ | \\ N \end{matrix}>C_6H_2(NO_2)_2.$$

This result points either to the conclusion that: (1.) True nitrosoazo-compounds do not exist, but are azimido-compounds or derivatives of the same; or that (2) nitrosoazo-compounds do exist, but on nitration are converted into azimido-compounds. If the latter conclusion is accepted, then on nitrating dinitrosoazo-compounds, the nitroso-group in the ortho-position relatively to the azo-group is reduced and thus becomes capable of converting the azo- into the azimido-group, and further the nitroso-group in the para-position to the azo-group is oxidised to the nitro-group. On treating mononitromononitroso- and dinitromononitroso-azobenzene with nitric and sulphuric acids, the author obtained tetranitrophenylazoximidobenzene, and not tetranitrophenylazimidobenzene. Against the assumption that nitroso-groups

of nitrosoazo-compounds are oxidised and reduced by boiling with nitro-sulphuric acid, is the fact that the nitroso-group of mononitroso-azo-compounds is not oxidised to a nitro-group by dilute nitric acid, by acetic and chromic acids, by fuming nitric acid, or by nitro-sulphuric acid, and that the nitroso-group of mononitrosoazo-compounds is not reduced by nitro-sulphuric acid. The author concludes that true nitrosoazo-compounds do not exist, but that they are derivatives of azimido-compounds.

The author reserves the study of the two isomeric dinitrophenyl-azimidobenzenes, nitrosoazoxybenzene and symmetrical trinitroso-phenylparabromazobenzene.

Tetranitrophenylazimidobenzene is prepared by boiling phenyl-azimidobenzene, dinitrosoazobenzene, or the two nitrodinitrosoazo-benzenes with 20 times the quantity of nitro-sulphuric acid. The mixture is poured into water and the precipitate extracted with alcohol and crystallised from toluene or acetic acid. From acetic acid, it separates in bright-yellow plates or prisms, and melts at 195—196°. It crystallises from toluene in long, thick prisms containing 2 mols. of toluene, and from benzene in yellowish-white needles containing 2 mols. of benzene. It is sparingly soluble in ether, alcohol, and chloroform.

Tetranitrophenylazoximidobenzene, $C_6H_3(NO_2)_2{\cdot}N_3O{:}C_6H_2(NO_2)_2$, is prepared in a similar way from nitronitroso- and dinitronitroso-azo-benzene. From acetone it is obtained in thin, well formed crystals, from acetic acid in small, measurable crystals, and large, yellow prisms, and from benzene in crystals containing 2 mols. of the hydrocarbon. It decomposes at 192°, is insoluble in ether, sparingly soluble in alcohol and chloroform, and very easily so in acetone. All the solutions are deep-yellow. E. C. R.

Metallic Derivatives of Phenylhydrazine. By G. Martina (*L'Orosi*, **15**, 37—41).—The metallic derivatives of phenylhydrazine described below were obtained by mixing solutions of a metallic salt (1 mol.) and phenylhydrazine (2 mols.). With zinc chloride, the salt $Zn(NHPh{\cdot}NH_2Cl)_2$ is formed. It crystallises in small, white needles which rapidly become brown or flesh-coloured. On adding hydrochloric acid to the mother liquor, no double salt is obtained, but only phenylhydrazine hydrochloride.

With mercuric chloride, a white, flocculent precipitate is formed from which metallic mercury is soon deposited even in the cold. Auric and platinic chlorides are likewise rapidly reduced by phenylhydrazine; baric and stannic chlorides are not acted on; stannous chloride is converted into the hydroxide, $Sn(OH)_2$. With cadmium sulphate, a yellowish or orange-coloured salt of the composition $Cd(NHPh{\cdot}NH_2)_2{\cdot}SO_4$ is obtained.

With ferrous sulphate, small, white needles or hard nodules of the composition $Fe(NHPh{\cdot}NH_2)_2{\cdot}SO_4$ are formed. They rapidly turn brown on exposure to the air.

Copper sulphate yields an unstable salt which almost immediately turns black; on warming, the copper is reduced to the metallic state. If the precipitated copper salt is thrown on a filter as soon as it is

formed, it swells up and rapidly decomposes with development of heat. With zinc sulphate, slender needles of the salt

$$Zn(NHPh{\cdot}NH_2)_2{\cdot}SO_4,$$

are obtained, soluble in water and in alcohol. On adding sulphuric acid to the mother liquor, the acid salt, $H_2SO_4.Zn(NHPh{\cdot}NH_2)_2{\cdot}SO_4$, is gradually deposited in hard, silvery plates which soon become rose-coloured. With nickel and strontium sulphates, no precipitates are formed. On adding an alcoholic solution of phenylhydrazine to an aqueous solution of lead nitrate, the basic salt, $Pb(OH)NO_3$, is precipitated.

Xylidine forms with zinc chloride the salt $Zn(C_6H_3Me_2{\cdot}NH_2Cl)_2$, which crystallises in tufts of white or pinkish needles, soluble in water and alcohol. It turns brown at 100°. On adding hydrochloric acid to the mother liquor, the hydrochloride of the base is formed. With zinc and cadmium sulphates, double salts are obtained, and on adding sulphuric acid to the mother liquors the acid salts are precipitated. No salts are formed with silver and copper nitrates, whilst with lead nitrate it behaves like phenylhydrazine.

S. B. A. A.

Action of Orthonitrobenzyl Chloride on Phenylhydrazine. By C. Paal and A. Bodewig (*Ber.*, **25**, 2896—2904).—Orthonitrobenzyl chloride and phenylhydrazine react with explosive violence; the action proceeds tranquilly, however, in the presence of a diluent. When the chloride (1 mol.) is added to a solution of phenylhydrazine (2 mols.) in absolute alcohol (4—5 vols.), and the mixture subsequently heated for 3—4 hours on the water-bath, phenylhydrazine hydrochloride separates, and, on adding the product to hot water containing acetic acid and sodium acetate, a red oil is precipitated which consists of orthonitrobenzylphenylhydrazine 50—60 per cent.), bisorthonitrobenzylphenylhydrazine (20—30 per cent.), and orthonitrophenylmethaneazobenzene (5 per cent.), together with a red resin. The oil is extracted with ether, and hydrochloric acid added to the solution, when the hydrochloride of the first-named compound is precipitated; the other two compounds (see below), being devoid of basic properties, remain dissolved, and are separated by fractional crystallisation from glacial acetic acid.

Orthonitrobenzylphenylhydrazine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPh{\cdot}NH_2$, crystallises from alcohol in yellow needles, melts at 72°, and is sparingly soluble in light petroleum, readily so in alcohol and ether; the *hydrochloride* melts at 196—198°, and is partially dissociated by a large excess of water. The *formyl* derivative, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPh{\cdot}NH{\cdot}CHO$, obtained by boiling the base for two hours with concentrated formic acid, crystallises from dilute alcohol in lustrous, bright-yellow, flat needles, melts at 141—142°, and is almost insoluble in light petroleum.

Orthamidobenzylphenylhydrazine, prepared by reducing the nitro-base with zinc dust and acetic acid, crystallises from dilute alcohol in flat, white needles or elongated leaflets, melts at 102°, boils at 254°, and is readily soluble in the usual solvents except light petroleum; solutions of its salts are not dissociated by water. The *formyl* derivative is obtained by treating formylorthonitrobenzylphenylhydrazine dissolved

in alcohol with zinc dust and hydrochloric acid at as low a temperature as possible; it crystallises from alcohol in small, white, stellate groups of tables, melts at 157°, and is almost insoluble in water and light petroleum; the formyl group is eliminated on heating with acids and alkalis, and when the compound is heated above its melting point, it yields an *anhydro-base*, $C_6H_4<^{CH_2\cdot NPh}_{N=CH}>NH$.

Bisorthonitrobenzylphenylhydrazine, $N_2HPh(CH_2\cdot C_6H_4\cdot NO_2)_2$, crystallises from alcohol in red needles, melts at 128°, and is sparingly soluble in ether and alcohol, readily so in benzene. It remains unaltered when boiled with acetic anhydride or when its solutions are heated with mercuric oxide, and yields, on reduction, amorphous substances which were not further examined.

Orthonitrophenylmethaneazobenzene, $NO_2\cdot C_6H_4\cdot CH_2\cdot N_2Ph$, is isolated from the final mother liquor obtained in crystallising the last-described compound; it crystallises from alcohol in dark red needles, melts at 154°, and on reduction with zinc dust and acetic acid, gives a *base*, $C_{13}H_{13}N_3$, which crystallises in flat, white needles, and melts at 218—220°; it is now being further investigated. A. R. L.

α-Phenylhydrazidopropionic Acid. By A. Reissert (*Ber.*, **25**, 2701—2705).—The compound described by the author (Abstr., 1884, 1152) as asymmetrical α-phenylhydrazidopropionic acid is, in accordance with v. Miller and Plöchl's statement (this vol., p. 1196), the symmetrical derivative obtained by Fischer and Jourdan (Abstr., 1884, 53), and subsequently by Japp and Klingemann (Trans., 1888, 535). The melting point previously given by the author (*loc. cit.*) is too high.

Ethyl phenylhydrazidopropionate, also described by the author (*loc. cit.*), is an oil which, if left for a time in the desiccator, undergoes oxidation to ethyl phenylhydrazinepyruvate. On boiling it with concentrated hydrochloric acid for four hours, α-anilidopropionic acid, phenylhydrazinepyruvic acid, and ammonia are produced.

α-Nitrosoanilidopropionic acid, NO·NPh·CHMe·COOH, is prepared by dissolving α-anilidopropionic acid (16·5 grams) in concentrated hydrochloric acid (14 grams), and, after diluting with water, adding to the cooled mixture a concentrated solution of potassium nitrite (8·5 grams). When purified by repeated dissolution in ammonia and reprecipitation with acid, it melts at 88·5° (corr.), and is very readily soluble in most solvents except light petroleum. The author hopes, by the reduction of this nitroso-derivative, to obtain the unknown asymmetrical α-phenylhydrazidopropionic acid. A. R. L.

Alkyl Derivatives of Hydroxylamine. By R. Behrend and E. König (*Annalen*, **271**, 92—94).—The authors describe further quantitative experiments, which afford additional proofs that the oxidation products of benzylnitrobenzylhydroxylamine and of nitrobenzylbenzylhydroxylamine are identical, and are formed in the same quantities in both cases (compare Abstr., 1891, 1032). F. S. K.

Quinoneoxime Ethers. By J. L. Bridge (*Amer. Chem. J.*, **14**, 276—286).—Quinoneoxime methoxide, $C_6H_4O{:}NOMe$, was prepared

by treating silver nitrosophenol suspended in ether with $1\frac{1}{4}$ times the calculated amount of methyl iodide. The dark brown, tarry mass obtained by spontaneous evaporation of the ethereal filtrate was extracted with hot light petroleum, and the solution decolorised with charcoal, when it yielded, on concentration, flat, yellow needles melting at 83° after recrystallisation. It dissolves readily in organic solvents and in hot water, and in considerable amount in cold water or light petroleum, has a strong, pleasant, ethereal odour, and is readily volatile with steam; if not quite pure, it quickly decomposes, like quinone, turning first green and then dark brown.

The same substance is formed by gently warming a solution of sodium nitrosophenol in methyl alcohol with methyl iodide. About 0·2 gram of dark red needles, probably a polymeric nitrosophenol, are obtained for each gram of nitrosophenol taken. This substance is insoluble in organic solvents, but dissolves in alkalis and ammonia with a deep red coloration, and is precipitated unchanged by acids or carbonic anhydride. It begins to decompose at 250° without melting. The analyses made did not yield concordant results, as it burns with very great difficulty. Nitric acid (sp. gr. 1·4) converts it quantitatively into 1 : 2 : 4-dinitrophenol melting at 114°. Tin and hydrochloric acid reduce it to paramidophenol melting at 180°.

The methoxide is quantitatively converted into a *dibromide*, $C_6H_4O{:}NOMe,Br_2$, by addition of bromine (1 mol.) to the chloroform solution. The reaction is complete in half an hour, and no hydrogen bromide is noticed. It is colourless, and crystallises from chloroform in four-sided plates, softens at 113°, and melts at 118° without decomposition.

Quinoneoxime ethoxide, $C_6H_4O{:}NOEt$, is obtained in a similar manner to the methoxide; it crystallises in yellow, rhombic or hexagonal plates, melts at 30°, and has a strong ethereal odour. It is easily volatile with steam, and dissolves readily in all solvents, being least soluble in cold water and light petroleum. The methoxide and ethoxide do not resemble nitrosophenol, but show a very close resemblance to benzoquinone. The conclusive proof that they are compounds of quinoneoxime, and not of nitrosophenol, is that α-benzylhydroxylamine converts quinone quantitatively into the compound $C_6H_4O{:}NO{\cdot}CH_2Ph$, which is identical in every respect with the compound obtained from sodium or silver nitrosophenol and benzyl chloride.

Quinoneoxime acetate, $C_6H_4O{:}NOAc$, is obtained by treating silver nitrosophenol suspended in much absolute ether with freshly-distilled acetic chloride. The compound formed crystallises in light yellow needles, and melts at 107°. It is but slightly soluble in water, and odourless; its solutions in ether and in alcohol are green, like those of nitrosophenol. If dry and finely powdered it causes sneezing.

Ethyl quinoneoximecarboxylate, $C_6H_4O{:}N{\cdot}O{\cdot}COOEt$, is obtained when silver nitrosophenol and ethyl chloroformate, in molecular proportion, are suspended in absolute ether, and gently heated for a short time; it crystallises in yellow plates melting at 110°.

Quinoneoxime benzoate, $C_6H_4O{:}NOBz$, is obtained by treating dry sodium or silver nitrosophenol with benzoic chloride, or, better, by shaking an alkaline solution of nitrosophenol with benzoic chloride.

It forms pale yellow needles melting at 172—174°. The solution in alcohol is green, but its colour is not so marked as that given by nitrosophenol or the acetate.

Quinoneoxime benzoxide, $C_6H_4O{:}NO{\cdot}CH_2Ph$, is formed when silver nitrosophenol, suspended in absolute ether, is heated for several hours with benzyl chloride ($\frac{3}{4}$ mol.) until the smell of the latter has disappeared; it crystallises in yellow, rectangular or rhombic plates and melts at 63·5°. The same substance is formed by heating sodium nitrosophenol dissolved in alcohol with benzyl chloride. It is insoluble in water, but readily soluble in all organic solvents except light petroleum. It has no odour. When treated with tin and hydrochloric acid, it is converted into paramidophenol, whilst much benzyl chloride is also formed. It is also obtained quantitatively by treating quinone (1 gram) dissolved in water (250 c.c.) with the calculated amount of α-benzylhydroxylamine hydrochloride dissolved in water containing a few drops of hydrochloric acid.

The results obtained show that the properties and stability of quinone and its derivatives depend entirely on the negative or positive condition of the molecule. W. T.

Action of Amido-Bases on Sodium Glyoxalsulphonate. By O. Hinsberg (*Ber.*, **25**, 2545—2547).—The author has already shown (Abstr., 1888, 372) that whereas aniline acts on sodium glyoxalsulphonate with formation of anilidoacetanilide, the naphthylamines yield sulphonic acids of naphthindoles. Benzylamine behaves in a similar manner to aniline, yielding the *benzylamide of benzylamidoacetic acid*, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CH_2Ph$, which forms an oil, but yields with hydrochloric acid a salt, crystallising in colourless plates. Ethyl-β-naphthylamine, on the other hand, yields *sodium ethyl-β-naphthindolesulphonate*, $C_{14}H_{12}NSO_3Na$, which crystallises in slightly yellowish needles, and is decomposed by hydrochloric acid with formation of a substance free from sulphur, the latter being probably *ethyl-β-naphthoxindole*, $C_{10}H_6{<}\overset{NEt}{\underset{CH_2}{>}}CO$. H. G. C.

Action of Acetic Chloride on Orthohydroxyaldehydes. By W. P. Bradley and F. B. Dains (*Amer. Chem. J.*, **14**, 293—300).—Parachlorosalicylaldehyde was dissolved in a slight excess of glacial acetic acid, and to it was added half its weight of acetic chloride. The reaction was immediate, with evolution of much heat; it was completed by heating on the water-bath after it had been left for some time. By pouring into water, dichlorodisalicylaldehyde, together with some unchanged chlorosalicylaldehyde, was precipitated; the latter substance was removed by treatment with dilute alkali. The yield averages 60—70 per cent. of the theoretical. From a hot concentrated solution in alcohol, fine, white, silky needles of dichlorodisalicylaldehyde were obtained; from more dilute solutions, it comes down in slender, mossy filaments. Its melting point is 172°. It is easily soluble in alcohol, ether, acetic acid, benzene, chloroform, and carbon bisulphide, less soluble in light petroleum. It easily dissolves

in concentrated sulphuric acid, giving an amber-coloured solution, which, when poured into water, deposits quantitatively parachlorsalicylaldehyde.

Dibromo- and dichloro-salicylaldehyde gave no condensation products with acetic chloride, even in a sealed tube at 115—130°.

Paranitrosalicylaldehyde, when treated in the same way as the chloro-compound, does not give a condensation product, but when heated at 100° in a sealed tube, a small quantity of dinitrosalicylaldehyde is obtained. It dissolves with difficulty in alcohol, acetic acid, ether, chloroform, carbon bisulphide, and light petroleum, and but little more freely in benzene. The sulphuric acid solution, when poured into water, gives paranitrosalicylaldehyde.

Orthonitrosalicylaldehyde appears to be unaffected by acetic chloride under any conditions.

α-Aldehydo-β-naphthol condenses very readily under the action of acetic chloride, with development of heat. The yield is nearly quantitative. The product, *β-diorthohydroxy-α-naphthaldehyde*, dissolves with difficulty in the ordinary solvents. From benzene or acetic acid, it is deposited in small, hard, nearly white crystals, melting at 241°. The solution in sulphuric acid is dark red, with a green fluorescence; on diluting it with water, α-aldehydo-β-naphthol is deposited.

Paramethylsalicylaldehyde gives a nearly quantitative yield of paradimethyldisalicylaldehyde. The pure compound melts at 141°; its molecular weight, determined by Raoult's method, using acetic acid as solvent, was 251·2; the calculated value is 254. It is easily soluble in most solvents, but dissolves sparingly in light petroleum. It crystallises from petroleum in beautiful, oblong tables, pointed at the ends. It is easily volatile with steam. Attempts to oxidise the methyl groups to carboxyl have failed; protracted boiling with a 15 per cent. alkaline solution of permanganate produced no effect.

Acetic chloride has no action on orthoaldehydosalicylic acid.

It appears probable that acetic chloride can secure the quantitative condensation of all orthohydroxyaldehydes in which only hydrocarbon groups are joined directly to the benzene ring. The introduction of negative groups hinders or entirely prevents condensation. The presence in the molecule of a chlorine or bromine atom reduces the yield 30—40 per cent. A single nitro-group in the para-position nearly prevents condensation, whilst a carboxyl- or nitro-group in the ortho-position, or the presence of two halogen atoms, prevents it altogether. W. T.

New Method for the Preparation of some Aromatic Nitroketones. By K. Lange and A. Zufall (*Annalen*, **271**, 1—11).—The compounds of the general formula $CCl_3{\cdot}CHR_2$, obtained by the condensation of chloral with aromatic hydrocarbons, are converted into unsaturated dichloro-compounds of the constitution $CCl_2{:}CR_2$ by alcoholic potash; when these unsaturated compounds are treated with nitric acid, they are decomposed, yielding, in some cases, not only unsaturated nitro-derivatives of the dichloro-compounds, but also

saturated nitro-ketones; a saturated nitro-ketone could not, however, be obtained from dichlorodixylylethylene, $CCl_2{:}C(C_6H_3Me_2)_2$.

A *dinitro* compound of the constitution $CCl_2{:}C(C_6H_4{\cdot}NO_2)_2$ is formed, together with dinitrobenzophenone, when dichlorodiphenylethylene is gradually added to well-cooled, concentrated nitric acid, the solution kept for a short time and then poured on to ice; the acid solution is decanted from the yellow, resinous precipitate, the latter extracted with hot alcohol, and the residue recrystallised from glacial acetic acid; in this way the dinitro-compound is obtained in yellow needles melting at 172°. From the acid mother liquors, dinitrobenzophenone is slowly deposited in crystals; this compound melts at 187—188°, and is identical with the paradinitrobenzophenone described by Städel and Haase (Abstr., 1890, 1422); it can be obtained by treating the dichlorodinitro-compound described above with concentrated nitric acid.

Dinitroditolyl ketone, $CO(C_6H_3Me{\cdot}NO_2)_2$, prepared by dissolving dichloroditolylethylene, $CCl_2{:}C(C_6H_4Me)_2$, in well-cooled concentrated nitric acid, crystallises from glacial acetic acid in yellow needles, melts at 144°, and dissolves freely in benzene and toluene, but is more sparingly soluble in acetone and alcohol, and insoluble in light petroleum. The *hydrazone*, $C_{21}H_{18}N_4O_4$, is a red, crystalline compound melting at 169—170°.

Diamidoditolyl ketone, $CO(C_6H_3Me{\cdot}NH_2)_2$, is formed when the dinitro-compound is treated with the theoretical quantity of stannous chloride in glacial acetic acid solution; it separates from dilute alcohol in yellow crystals and melts at 171—172°. The *diacetyl* derivative, $C_{19}H_{20}N_2O_3$, crystallises in colourless needles and melts at 196—197°. The *dipiperidide*, $CO(C_6H_3Me{\cdot}N{:}N{\cdot}NC_5H_{10})_2$, prepared by treating the diazotised diamido-compound with piperidine, crystallises from alcohol and acetone in yellowish-red needles.

When dichloroditolylethylene is oxidised with chromic acid in glacial acetic acid solution, it yields paratolylbenzoic acid (m.p. 224—225°), so that in the dinitro-ketone described above the methyl groups are in the para-position relatively to the carbonyl radicle. A hydroxyketone of the composition $CO(C_6H_3Me{\cdot}OH)_2$ is formed when a sulphuric acid solution of diamidoditolyl ketone is diazotised and the mixture then boiled; it sublimes in lustrous plates, but without melting. When this dihydroxy-ketone is fused with potash, it is converted into a hydroxytoluic acid, $C_8H_8O_3$, which melts at 206—207°, and does not give a coloration with ferric chloride; the constitution of this acid is probably [COOH : OH : Me = 1 : 3 : 4] and consequently that of the dinitro-ketone [CO : NO_2 : Me = 1 : 3 : 4].

F. S. K.

Iodosobenzoic Acid. By V. Meyer and W. Wachter (*Ber.*, **25**, 2632—2635).—Orthiodobenzoic acid dissolves in fuming nitric acid with evolution of heat; on heating the solution for some seconds, cooling, and pouring into water, a precipitate of *iodosobenzoic acid*, $C_7H_5IO_3$, separates, and, when crystallised from boiling water, is obtained in satiny leaflets or granular crystals which melt at 209°, with evolution of gas. The acid acts as a strong oxidising agent, and may be estimated by heating in a closed tube at 100° with

potassium iodide and dilute sulphuric acid in the absence of air, iodobenzoic acid and iodine are thus liberated, and the latter, on titration with standard thiosulphate solution, indicates the amount of the new acid present. On heating with concentrated hydrochloric acid, chlorine is liberated. When dissolved in ammonia solution and warmed with zinc-dust, it readily yields benzoic acid. The acid forms salts with alkalis, and dissolves in aqueous ammonia; on adding ammoniacal silver nitrate to this solution, however, pure iodosobenzoic acid is reprecipitated. Its constitution may be represented either as

$$COOH\cdot C_6H_4\cdot I{:}O \text{ or as } \begin{array}{l} CH \\ CH \\ CH \end{array}\!\!\begin{array}{l} \diagup\!\!\diagdown \\ \| \\ \diagdown\!\!\diagup \end{array}\!\!\begin{array}{l} CH \\ O \\ CH \end{array}\!\!\begin{array}{l} \diagdown \\ \| \\ \diagup \end{array}\!\!\begin{array}{l} CI \\ C\cdot COOH \end{array};$$

the former is, however, the more probable constitution. The acid decolorises permanganate solution, and, when warmed with aniline or orthamidobenzoic acid dissolved in glacial acetic acid, deep brown solutions are obtained. The reactions involved in these changes are under examination.

Orthobromobenzoic and meta- and para-iodobenzoic acids, on treatment with fuming nitric acid, simply undergo nitration.

W. J. P.

Hexachlorometadiketohexene. The Action of Chlorine on 1, 3, 5-Dihydroxybenzoic Acid. By T. Zincke and O. Fuchs. (*Ber.*, **25**, 2680—2698).—Dichloro- and trichloro-dihydroxybenzoic acids are obtained when dihydroxybenzoic acid, dissolved in acetic acid, is treated with the quantity of chlorine requisite to form the trichloro-acid. The two acids cannot be separated by fractional crystallisation, but the acetyl compounds are easily separated by crystallisation from a mixture of benzene and light petroleum, in which the trichloro-derivative is sparingly soluble.

Hexachlorometadiketohexene is easily prepared by saturating a mixture of dihydroxybenzoic acid (1 part) and acetic acid (5 parts) with dry chlorine, allowing the mixture to remain 24 hours, again saturating with chlorine, and allowing it to remain 24 hours, and distilling off the acetic acid at 90—100° under diminished pressure. The crude compound is purified by distillation under a pressure of 11—15 mm.

2 : 4- or 2 : 6-*Dichlorodihydroxybenzoic acid*, $C_6HCl_2(OH)_2\cdot COOH$, crystallises in short, colourless needles, melts at 202°, and is sparingly soluble in light petroleum and hydrochloric acid, but easily in other solvents. The *acetyl* compound crystallises in beautiful, colourless crystals, and melts at 179°.

Trichlorodihydroxybenzoic acid, $C_6Cl_3(OH)_2\cdot COOH$, crystallises in slender, white needles, melts at 192°, and is easily soluble in alcohol, ether, benzene, and water. The *acetyl* compound crystallises in slender needles, and melts at 207°. The *methyl* salt of the acetyl compound crystallises from dilute alcohol in thick, colourless needles, and melts at 116°.

Hexachlorometadiketohexene, $CO<\begin{matrix} CCl_2\cdot CO \\ CCl{:}CCl \end{matrix}>CCl_2$, a colourless, crystalline mass, melts at 115°, distils at 159—160° under 13—15 mm.,

has a penetrating odour, causing tears, and is easily soluble in ether benzene, and chloroform, sparingly so in light petroleum. When boiled with water, it yields a ketone of the formula $C_5H_2Cl_6O$. It liberates iodine from potassium iodide, yields tetrachlororesorcinol when reduced, is not attacked by chlorine at 180—200°, does not give a characteristic compound with aniline, and with ammonia yields the acid amide $C_6HCl_6O_2{\cdot}NH_2$. When treated with phosphorus pentachloride, it yields hexachlorobenzene and the ethereal salt

$$C_6Cl_5O{\cdot}PO(OH)_2$$

(m. p. 203°).

Tetrachlororesorcinol, $C_6Cl_4(OH)_2$, is obtained by reducing the hexachlorodiketone, dissolved in 10 parts of acetic acid, with stannous chloride. It crystallises in long, colourless needles, melts at 141°, is easily soluble in alcohol, ether, benzene, and acetic acid, somewhat easily in hot water, and sparingly in dilute hydrochloric acid. The authors were unable to obtain a quinone from it. The *acetyl compound* crystallises in white needles, melts at 145°, is insoluble in water, and tolerably soluble in acetic acid, ether, alcohol, and benzene.

Dichloracetyltetrachlorocrotonic acid,

$$CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH,$$

is obtained by adding a cold solution of the hexachloroketone in acetic acid (5 to 6 parts) to 4—5 times the volume of sodium acetate (1 part salt to 10 parts water). The mixture is allowed to remain a few minutes, strongly acidified with hydrochloric acid, and the product crystallised from hot petroleum. It crystallises in long, colourless scales, melts at 112°, is easily soluble in ether, alcohol, and benzene, sparingly in water, and, when heated with water, yields the ketone, $C_5Cl_6OH_2$; the latter is also obtained by dry distillation of the acid. When treated with aniline, carbonic anhydride is evolved, and the anilide, $C_5H_2Cl_5O{\cdot}NHPh$, is formed. The *methyl* salt crystallises in colourless tablets, melts at 93°, and is easily soluble in alcohol, ether, &c. The *amide*, $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}CONH_2$, is obtained by passing ammonia into a solution of the hexachloroketone in benzene. It crystallises in white, silky needles, melts at 181°, and is easily soluble in alcohol and acetic acid.

The *ketone*, $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CHCl_2$, is obtained by diluting with water an acetic acid solution of the preceding acid, and distilling the mixture with steam as long as oil comes over, or by boiling the acid with water in a reflux apparatus as long as carbonic anhydride is evolved, and distilling with superheated steam; or by heating the acid by itself and distilling the product under diminished pressure. It is a yellow, highly refractive oil, boils at 147—148° under a pressure of 20—25 mm., and has a penetrating odour, causing tears.

The *azine*, $C_5H_2Cl_5{<}\overset{N-}{NH}{>}C_6H_4$, is obtained if an alcoholic solution of the ketone and orthophenylenediamine is left for a time at the ordinary temperature; it crystallises in broad, yellow needles, melts at 126°, and is insoluble in water, tolerably soluble in hot acetic acid, ether and benzene, and less so in alcohol or petroleum. The *anilide*,

$C_5H_2Cl_5O{\cdot}NHPh$, is obtained by adding excess of aniline to a solution of the ketone in acetic acid; it crystallises in short, lustrous, yellow needles, melts at 89°, and is easily soluble in ether, acetic acid, benzene, and light petroleum, less so in alcohol, and insoluble in water.

Trichloroacetyltetrachlorocrotonic acid,

$$CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH,$$

is obtained by treating the hexachlorometadiketone with a dilute solution of chloride of lime. It crystallises from hot petroleum in colourless scales or thick needles, from a mixture of ether and petroleum in large, lustrous, monoclinic crystals, melts at 117°, and is easily soluble in alcohol, ether, benzene, and acetic acid, sparingly so in water and petroleum. When boiled with water, carbonic anhydride is evolved, and the ketone C_5HCl_7O is formed. With aniline, it yields the anilide $C_5HCl_6O{\cdot}NHPh$, and is decomposed by alkalis and acids yielding chloroform and the bibasic acid $C_5H_2Cl_4O_4$. When heated alone, it yields the pentene-ketone C_5Cl_6O, together with other products. The *methyl salt* crystallises in thick, colourless scales, melts at 90°, and is easily soluble in the ordinary solvents.

The *ketone*, $CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CHCl_2$, is obtained by heating the preceding compound with water. It is a bright yellow, strongly refractive liquid, boils at 182—185° under 13—15 mm. pressure, and has a penetrating smell, causing tears. When treated with alkali, it yields chloroform and an acid which is probably a tetrachlorocrotonic acid. The *azine*, $C_5HCl_6{\lessdot}^{N-}_{NH}{>}C_6H_4$, crystallises from alcohol in yellow needles, melts at 149°, and is tolerably soluble in benzene, ether, and acetic acid, less so in petroleum and alcohol, and insoluble in water. The *anilide*, $C_5HCl_6O{\cdot}NHPh$, crystallises from hot alcohol in beautiful, yellow needles, melts at 134°, and is somewhat sparingly soluble in alcohol and light petroleum, more so in ether, benzene, and acetic acid.

The ketonic acid $C_6HCl_7O_3$, when heated under the ordinary pressure, yields compounds of the formula C_5Cl_6O, and, by distilling the product under diminished pressure, a colourless, refractive oil is obtained which boils at 148—150° under 12—15 mm. pressure. If the oil is distilled a few times under the ordinary pressure, and then left for a time, colourless crystals are obtained which are identical with those of the isomeric ketone described by Küster and Zincke (*Ber.*, **23**, 2207). The oil dissolves in sodium hydroxide, with an odour of chloroform. When hydrochloric acid is added to the alcoholic solution, pentachloropentolic acid, $C_5Cl_5HO_2$, is formed.

Tetrachloroglutaconic acid, $COOH{\cdot}CCl_2{\cdot}CCl{:}CCl{\cdot}COOH$, is obtained by dissolving the acid $C_6HCl_7O_3$ in sodium carbonate, and adding a dilute solution of sodium hydroxide as long as a turbidity is produced; the mixture is then acidified with hydrochloric acid and extracted with ether. It crystallises in colourless tablets and plates, melts at 109—110°, and is easily soluble in the ordinary solvents, with the exception of petroleum. The *ammonium*, *barium*, and *calcium salts* are easily soluble. The *methyl salt* is a liquid. E. C. R.

$\alpha\beta$-Dichlorocinnamic Acid (Phenylpropiolic Acid Dichloride). By C. Nissen (*Ber.*, **25**, 2664—2667).—$\alpha\beta$-Dichlorocinnamic acid, CPhCl:CCl·COOH, is prepared as described by Roser and Haseloff (*Annalen*, **247**, 146) by passing chlorine into a chloroform solution of phenylpropiolic acid as long as it is absorbed. Roser and Haseloff have only prepared the crude acid. The pure acid is obtained by drying the crude product on porous plates and precipitating it from the chloroform solution by petroleum. It crystallises in beautiful leaflets, has a very faint odour, melts at 120—121°, is easily soluble in alcohol, ether, chloroform, benzene, and acetic acid, but insoluble in light petroleum and cold water. When pure, it yields a colourless solution with soda, but a trace of impurity causes the solution to turn purplish-red. The author was unable to obtain a stereoisomeric acid from the crude product similar to the acid obtained by Roser and Haseloff by the action of bromine on phenylpropiolic acid. By extracting with ether the porcelain plates used in the purification, an oil is obtained which is completely soluble in soda, but is not a dichlorocinnamic acid. The *ammonium salt* crystallises in long needles. The solution of the salt gives no precipitate with calcium, barium, or magnesium salts ; with lead acetate, it gives a white precipitate. The *silver salt* crystallises in white needles, and is soluble in boiling water. The *methyl salt* is a colourless oil. The author was unable to obtain allocinnamic acid by eliminating the chlorine from dichlorocinnamic acid. The chlorine is only eliminated by boiling with zinc and alcohol for 20 hours, and the acid thus obtained is cinnamic acid. Under these conditions, if allocinnamic acid were formed, it would be converted into cinnamic acid.

The author has obtained β-dibromocinnamic acid in beautiful, yellow prisms. The crystals belong to the rhombic system ; $a : b : c = 0{\cdot}9573 : 1 : 0{\cdot}5244$. E. C. R.

Asymmetrical Amidoisophthalic Acid. By R. Loewenherz (*Ber.*, **25**, 2795—2798).—The author endeavoured to obtain an acid of the constitution $C_{12}H_6(NH_2)_2(COOH)_2$, by the oxidation of acetylorthotolidine, but obtained instead, asymmetrical *acetylamidoisophthalic acid*, $NHAc{\cdot}C_6H_3(COOH)_2$, which separates from hot water in colourless crystals, decomposes at 270°, is sparingly soluble even in hot water, but more readily in alcohol. When hydrolysed with a mixture of 3 vols. of sulphuric acid and 2 vols. of water, it is converted into *amidoisophthalic acid*, $NH_2{\cdot}C_6H_3(COOH)_2$, which melts above 300°, and on diazotisation and boiling with water yields the hydroxyisophthalic acid described by Jacobsen (Abstr., 1878, 583). The same acetylamidoisophthalic acid was obtained by Hofmann (this Journ., 1877, i, 90) from metaxylidine, but he was unable to hydrolyse it with hydrochloric acid, whereas the hydrolysis proceeds readily with sulphuric acid of the strength given above.

As the oxidation did not yield diphenyldiamidodicarboxylic acid, the author prepared this acid from orthonitrobenzoic acid (compare Griess, Abstr., 1888, 589), which was boiled with aqueous potash and zinc dust until colourless, and the resulting hydrazo-compound converted into the isomeric *diphenyldiamidodicarboxylic acid*,

$C_{12}H_6(NH_2)_2(COOH)_2$ [= 2 : 2′ : 4 : 4′], by means of boiling hydrochloric acid. This compound has very feebly basic properties, the salts with acids being decomposed by water. An attempt was made to convert it into a diphenyltetracarboxylic acid by means of Sandmeyer's reaction, but without success; this acid has, however, been obtained by the oxidation of ditolyldicarboxylic acid, and will be described in a later paper. H. G. C.

Chlorodurenesulphonic Acid. By A. Töhl (*Ber.*, **25**, 2759—2761).—The author finds that, like sulphuric acid (this vol., p. 968), crystalline fuming sulphuric acid yields with chlorodurene, chloropentamethylbenzene and chlorotrimethylbenzenesulphonic acid. By the action of chlorosulphuric acid on chlorodurene, *chlorodurenesulphonic acid*, $C_{10}H_{12}Cl{\cdot}SO_3H$, is formed. This crystallises from benzene in scales, melting at 136°. The *barium* salt with 1 mol. H_2O is sparingly soluble in water, forms six-sided rhombic plates, and melts with decomposition at 150°. The *potassium* salt with 1 mol. H_2O gives sparingly soluble scales, the *sodium* salt scales free from water. The *sulphochloride* crystallises from light petroleum in six-sided rhombic plates melting at 53—54°, the *sulphonamide* in scales melting at 180—181°. During the preparation of the acid, a compound was obtained composed of 1 mol. sulphonic acid and 2 mols. sulphochloride in the form of short needles melting at 91—92°. L. T. T.

Formation of Substituted Indoles. By A. Bischler (*Ber.*, **25**, 2860—2879).—The author concludes from the experiments to be described that the formation of 2′-phenylindole from phenylacetanilide and aniline (Möhlau, Abstr., 1883, 342; E. Fischer and Schmitt, *ibid.*, 1888, 698) takes place as follows:—

$$COPh{\cdot}CH_2{\cdot}NHPh + C_6H_5NH_2 =$$

$$H_2O + CPh(NHC_6H_5){:}CH{\cdot}NHPh = CPh\lessdot^{CH}_{NH}\gtrdot C_6H_4 + NH_2Ph.$$

Phenylacetanilide, prepared by triturating bromacetophenone (1 mol.) with aniline (2 mols.) and alcohol, agrees with Möhlau's description (*loc. cit.*). *Phenylacetorthotoluidide*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me$, obtained in the same manner from bromacetophenone and orthotoluidine, separates from benzene in flat, yellow crystals, and melts at 89°; the *hydrochloride* forms colourless needles, and decomposes when boiled with water; whilst the *acetyl* derivative, $COPh{\cdot}CH_2{\cdot}NAc{\cdot}C_6H_4Me$, crystallises in white needles, and melts at 92°. *Phenylacetoparatoluidide* crystallises from alcohol in bright yellow prisms, melts at 127°, and yields an *acetyl* derivative melting at 89°. *Phenylacetometachloranilide*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Cl$, prepared from bromacetophenone and metachloraniline, forms faintly yellow, felted needles, and melts at 138°; the *acetyl* derivative melts at 82°.

2′-Phenylindole is obtained by boiling either phenylacetanilide or phenylacetorthotoluidide with aniline; the nitroso-derivative melts at 247° (compare Fischer and Schmitt, *loc. cit.*). 1-*Methyl*-2′-*phenylindole* is formed when either phenylacetanilide or phenylacetortho-

toluidide is boiled with orthotoluidine. It boils at 250° (10 mm.); the distillate solidifies, and when crystallised from alcohol, the compound melts at 118—119°; it gives a violet-blue pine splinter reaction. The *picrate* melts at 126°, and the *nitroso*-derivative melts at 232°. Phenylacetoparatoluidide, when heated with orthotoluidine, yields a methylphenylindole melting at 112·5°. 3-*Methyl*-2′-*phenylindole* is obtained by boiling either phenylacetanilide or phenylparatoluidide with paratoluidine. It crystallises from benzene or alcohol in white leaflets, melts at 213°, and gives a violet-blue pine splinter reaction; the *picrate* melts at 135°, and the nitroso-derivative at 262°.

2′-*Phenylchlorindole* [Cl = 2 or 4] is obtained from phenylacetylmetachloranilide (1 mol.), and metachloraniline (2 mols.), or from phenylacetylorthotoluidide (1 mol.), and metachloraniline (2 mols.). It forms small leaflets, melts at 181—182°, gives a violet-blue pine splinter reaction, and is almost insoluble in light petroleum. The *picrate* melts at 127°, and the *nitroso*-derivative melts at 228—229°.

A. R. L.

Carbazole. By G. Pulvermacher and W. Loeb (*Ber.*, **25**, 2766—2767).—By heating a 40 per cent. formaldehyde solution, or trioxymethylene, with carbazole in closed tubes at 100°, the authors obtained *methylenecarbazole*, $CH_2(NC_{12}H_8)_2$, crystallising in long, white, silky needles, which are still solid at 280°. It is a very stable, basic substance, soluble in boiling aniline, but insoluble in the usual solvents. The *picrate* is crystalline. It is not decomposed by concentrated hydrochloric acid even at 190°. Strong nitric acid yields a *tetranitro*-derivative soluble in glacial acetic acid, from which it crystallises in yellow scales. It is acid in properties, forming red crystalline *sodium* and *potassium* derivatives. Zinc and acetic acid appear to cause the reduction of all four nitro-groups.

L. T. T.

Orthotolidinedisulphonic Acid. By J. Helle (*Annalen*, **270**, 359—375).—The compounds described in this paper were prepared by methods similar to those employed by Limpricht (Abstr., 1891, 929) and Limpricht and Meyer (this vol., p. 973), in the case of the benzidine derivatives.

Orthotolidinedisulphonic acid,

$$\overset{6}{SO_3H}\cdot C_6H_2\overset{3}{Me}(\overset{4}{NH_2})\cdot C_6H_2\overset{3'}{Me}(\overset{4'}{NH_2})\cdot\overset{6'}{SO_3H},$$

is obtained by heating orthonitrotoluenesulphonic acid with soda and zinc dust until the solution becomes colourless; it crystallises in colourless, microscopic needles, containing when air dried $1\frac{1}{2}$ mols. H_2O, and is insoluble in alcohol, ether, and glacial acetic acid, and only very sparingly soluble in hot water (compare Bender and Schultz, Abstr., 1887, 268). The potassium hydrogen salt crystallises in needles with 3 mols. H_2O; the barium salt crystallises with 5 mols. H_2O. The *tetrazo*-derivative, $C_{14}H_{10}N_4S_2O_6$, crystallises in well-defined microscopic needles, explodes at 86°, and is almost insoluble in cold water; it seems to crystallise with 1 mol. H_2O.

Ditolyldisulphonic acid, $SO_3H\cdot C_6H_3Me\cdot C_6H_3Me\cdot SO_3H$, is obtained when the tetrazo-derivative just mentioned is boiled with alcohol

and finely-divided copper; it crystallises in yellowish needles, and is very readily soluble in water, but more sparingly in alcohol, and insoluble in ether. The normal *potassium* salt forms readily soluble, hexagonal, anhydrous plates, but the acid salt contains water of crystallisation. The *barium* salt, $C_{14}H_{12}S_2O_6Ba + 5H_2O$, crystallises in rhombic plates, and is rather sparingly soluble in water. The *chloride*, $C_{14}H_{12}S_2O_4Cl_2$, separates from chloroform or benzene in well-defined rhombic prisms, and melts at 228—229°. The *amide*, $C_{14}H_{12}S_2O_4(NH_2)_2$, crystallises from alcohol, in which it is only sparingly soluble, in microscopic needles, which seem to contain 1 mol. C_2H_6O; it decomposes at a temperature above 360°, but without melting.

A *tolidinesulphonic acid*, which has probably the constitution $SO_3H\cdot C_6H_2^{6}Me^{3}(NH_2)^{5}\cdot C_6H_2^{3'}Me^{5'}(NH_2)^{6'}\cdot SO_3H$, is obtained when barium ditolyldisulphonate is treated with concentrated nitric acid and the product reduced with ammonium sulphide; it crystallises from water, in which it is readily soluble, in colourless, well-defined needles. The *barium* salt, $C_{14}H_{14}N_2S_2O_6Ba + 4H_2O$, crystallises in yellowish needles, and is only sparingly soluble in boiling water. The *potassium* salt crystallises in plates, and is very readily soluble. When the barium salt is heated with lime, it seems to yield metatolidine.

Dicresol, $OH\cdot C_6H_3Me\cdot C_6H_3Me\cdot OH$, prepared from ditolyldisulphonic acid in the usual manner, crystallises in colourless needles, melts at 143°, and is readily soluble in alkalis.

Dicresoldisulphonic acid, $SO_3H\cdot C_6H_2Me(OH)\cdot C_6H_2Me(OH)\cdot SO_3H$, prepared by heating the tetrazo-derivative described above with a large quantity of water, is a crystalline substance very readily soluble in water, alcohol, and glacial acetic acid, but insoluble in ether and chloroform. The *potassium* salt, $C_{14}H_{12}S_2O_8K_2 + 3H_2O$, crystallises in colourless needles, and is very readily soluble in water. The *barium* salt crystallises in well-defined, rhombic plates with 8 mols. H_2O, and effloresces on exposure to the air.

Dihydrazineditolyldisulphonic acid,

$$SO_3H\cdot C_6H_2Me(N_2H_3)\cdot C_6H_2Me(N_2H_3)\cdot SO_3H,$$

obtained by reducing the tetrazo-compound with stannous chloride, is a yellowish, crystalline powder, very sparingly soluble in hot water; it turns yellowish-brown when heated at 100° and when exposed to the light, and is then very readily soluble in water, some decomposition having taken place with evolution of nitrogen. The *barium* salt, $C_{14}H_{16}N_4S_2O_6Ba$, seems to crystallise with 5 mols. H_2O, and is decomposed by boiling water with evolution of nitrogen.

The *diazo*-derivative, $SO_3H\cdot C_6H_2Me(NH_2)\cdot C_6H_2Me<\begin{matrix}N:N\\SO_3\end{matrix}>$ crystallises in yellowish needles, is only sparingly soluble in cold, and is decomposed by hot water with evolution of nitrogen.

Amidoditolyldisulphonic acid, $SO_3H\cdot C_6H_2Me(NH_2)\cdot C_6H_3Me\cdot SO_3H$, crystallises in slender needles, and is readily soluble in water, but only sparingly in dilute alcohol. The *barium* salt, $C_{14}H_{13}NS_2O_6Ba + 5H_2O$, crystallises in yellowish-red plates, and is only sparingly

soluble in water. The *potassium* salt is readily soluble, and crystallises in prisms.

Amidohydroxyditolyldisulphonic acid,

$$SO_3H\cdot C_6H_2Me(OH)\cdot C_6H_2Me(NH_2)\cdot SO_3H,$$

crystallises in almost colourless needles, and is very readily soluble in water, but insoluble in alcohol and ether. The *barium* salt, $C_{14}H_{13}NS_2O_7Ba + 4\frac{1}{2}H_2O$, crystallises in reddish plates, and is moderately easily soluble in water; the *potassium* salt and the *calcium* salt crystallise in prisms, and are readily soluble; the *silver* salt is crystalline.

Hydrazineamidoditolyldisulphonic acid,

$$SO_3H\cdot C_6H_2Me(N_2H_3)\cdot C_6H_2Me(NH_2)\cdot SO_3H,$$

prepared by reducing the corresponding diazo-compound with stannous chloride, is a yellowish, semi-crystalline powder, sparingly soluble in water. The *barium* salt, $C_{14}H_{15}N_3S_2O_6Ba + 6H_2O$, crystallises in golden needles, and decomposes when heated above 110°.

Hydrazotoluenedisulphonamide,

$$NH_2\cdot\overset{4}{S}O_2\cdot C_6H_3\overset{1}{M}e\cdot\overset{2}{N}H\cdot\overset{2}{N}H\cdot C_6H_3\overset{1}{M}e\cdot\overset{4}{S}O_2\cdot NH_2,$$

is obtained when orthonitrotoluene-parasulphonamide is warmed with ammonia and zinc dust; it crystallises from hot water in long, colourless needles, and from glacial acetic acid and alcohol in prisms melting at 221—222°. It is almost insoluble in cold water and only sparingly soluble in ammonia, but readily in alcohol and potash; its alkaline solutions turn red on exposure to the air. The *potassium* derivative is deposited in almost colourless crystals when a solution of the acid in alcoholic potash is precipitated with ether and kept for some time in a closed vessel; it is stable in the air. The *diacetyl* derivative, $C_{18}H_{22}N_4S_2O_6$, prepared by boiling the hydrazo-compound with acetic anhydride, crystallises from alcohol in colourless needles, and melts at a very high temperature.

Azotoluenedisulphonamide is formed, together with tolidinedisulphonamide and amidotoluenesulphonamide (m. p. 175°), when the hydrazo-compound is heated with hydrochloric acid; it forms red crystals, and melts at 319·5°. The *potassium* derivative, $C_{14}H_{14}N_4S_2O_4K_2$, crystallises in intensely red, flat needles, and is decomposed by acids yielding azotoluenedisulphonamide.

Tolidinedisulphonamide,

$$NH_2\cdot SO_2\cdot C_6H_2Me(NH_2)\cdot C_6H_2Me(NH_2)\cdot SO_2\cdot NH_2,$$

crystallises from hot water in well-defined needles, melts at 304·5°, and is almost insoluble in cold water and only sparingly soluble in alcohol. When heated with concentrated hydrochloric acid at 150°, it is converted into the corresponding disulphonic acid. The *hydrochloride*, $C_{14}H_{18}N_4S_2O_4,2HCl + 2H_2O$, separates from water in lustrous needles, and from alcoholic ether as a colourless, crystalline powder melting at 284—285°: it is readily soluble in water and alcohol. The

sulphate, $C_{14}H_{18}N_4S_2O_4,H_2SO_4$, forms lustrous plates, and is more sparingly soluble in water than the hydrochloride. The *sodium* derivative, $C_{14}H_{16}N_4S_2O_4Na_2$, prepared by adding alcoholic ether to a solution of the amide in dilute soda, is a colourless, crystalline compound, very readily soluble in water. F. S. K.

Hydroxyaurin and Hydroxyaurincarboxylic Acids. By N. Caro (*Ber.*, **25**, 2671—2675).—The compounds described in this paper were prepared by the method previously described by the author (this vol., p. 855).

Hydroxyaurindicarboxylic acid, $O<\begin{matrix}C_6H_3\cdot OH\\ |\\ C[C_6H_3(OH)\cdot COOH]_2\end{matrix}$, separates from alcohol as a red, microcrystalline powder, decomposes at 140°, is easily soluble in alcohol, sparingly so in water, and soluble in ether. The barium, calcium, lead, aluminium, and iron salts are sparingly soluble or insoluble in water, and are dark-red to reddish-blue. The *calcium salt*, $C_{21}H_{12}O_8Cu$, is obtained by precipitating the ammoniacal solution of the free acid with calcium chloride.

Dihydroxyaurindicarboxylic acid is obtained by the condensation of methylenediresorcylic acid with phenol.

Trihydroxyaurindicarboxylic acid is obtained from methylenediresorcylic acid and resorcinol. It crystallises in microscopic leaflets, is soluble in hot water and alcohol, and insoluble in ether and benzene.

The condensation products of methylenedisalicylic acid or methylenediresorcylic acid with pyrogallol could not be obtained pure.

Methylenedigallic acid and phenols give bad yields, and the products are very difficult to purify owing to the ease with which they oxidise both in alkaline and aqueous solution.

Tetrahydroxyaurindicarboxylic acid, $O<\begin{matrix}C_6H_4\\ |\\ C[C_6H(OH)_3\cdot COOH]_2\end{matrix}$, prepared from methylenedigallic acid, is a reddish-violet powder which is soluble in alcohol, hot water, and alkalis, but insoluble in cold water.

Pentahydroxyaurindicarboxylic acid, $O<\begin{matrix}C_6H_3\cdot OH\\ |\\ C[C_6H(OH)_3\cdot COOH]_2\end{matrix}$, is obtained by the condensation of methylenedigallic acid and resorcinol in a solution of concentrated sulphuric acid (1 part) and acetic acid (1 part) at 5—7°.

The aurindicarboxylic acids give dyes with mordants; they are weaker and less beautiful than those from the tricarboxylic acids. The presence of resorcylic acid causes an orange shade, and of gallic acid a brown shade. Derivatives of methylenedigallic acid dye badly, owing to the ease with which they are oxidised. With regard to the absorption spectra, derivatives of salicylic acid exhibit an absorption between D and *b*; derivatives of resorcinol and resorcylic acid an absorption between *b* and F; mixed derivatives show dark bands in both positions.

Lastly, the author has made experiments to determine if an increase in the number of hydroxyl groups in aurin gives compounds capable of yielding colours with mordants.

The trihydroxyaurin described by Nencki and Schmid (*J. pr. Chem.*, **23**, 547) was prepared, and did not give dyes with mordants.

Hexahydroxyaurin (pyrogallaurin), $O<\begin{matrix}C_6H_2(OH)_2\\ |\\ C[C_6H_2(OH)_3]_2\end{matrix}$, is obtained by heating a mixture of pyrogallol (3 parts), formic acid (1 part), and zinc chloride (1 part) for 4 hours at 80°. It is a red, extremely hygroscopic powder, is easily soluble in alcohol and water, insoluble in ether, and oxidises very readily both in aqueous and alkaline solution. It yields dyes with mordants. E. C. R.

A New Synthesis of Diphenylene Oxide. By E. Täuber and E. Halberstadt (*Ber.*, **25**, 2745—2746).—The substance obtained by Täuber (Abstr., 1891, 570) by boiling the tetrazo-derivative of orthodiamidophenyl with water was compared with Graebe's diphenylene oxide and found to be identical. The yield of the oxide is about 70 per cent. of the diamine used. L. T. T.

Action of Aniline on Benzile. By M. Siegfeld (*Ber.*, **25**, 2600—2601).—Benzilemonanil was prepared by Voigt (Abstr., 1886, 887) by heating benzile with excess of aniline in a sealed tube at 200°; the benzile does not all react, but on heating for nine hours at 220°, benzanilide and benzaldehyde are produced.

Benziledianil, NPh:CPh·CPh:NPh, is obtained by heating a mixture of benzile (5 grams) and aniline with phosphoric anhydride for 6 hours in a sealed tube at 200°. A dark, solid mass and a thick, brown liquid are thus got; the latter, on crystallisation from alcohol, yields the dianil (2 grams) in brilliant, yellow leaflets which melt at 141—142°. It is soluble in chloroform, less so in benzene, and sparingly soluble in alcohol, ether, and light petroleum.

W. J. P.

Benzileoximes. By K. Auwers and M. Siegfeld (*Ber.*, **25**, 2597—2599).—*Benzileoximeanil*, OH·N:CPh·CPh:NPh, is prepared by heating benzile α- or γ-oxime with aniline in alcoholic acetic acid solution, and crystallises in colourless needles melting at 211—212°. The *acetyl derivative* is formed by the action of acetic anhydride on the preceding compound, and is deposited in small, yellow plates which melt at 135—136°. Attempts to obtain the same substance by the action of aniline on the acetyl derivatives of the oximes were unsuccessful.

Benzileoximeparatoluidil is prepared in a similar manner to the anil, which it closely resembles; in both cases the α-oxime reacts more readily than the γ-oxime; the same compound is also formed by the action of hydroxylamine hydrochloride on benzileditoluidil,

$$C_6H_4Me\cdot N:CPh\cdot CPh:N\cdot C_6H_4Me,$$

at ordinary temperatures, and is deposited in colourless, acicular crystals which melt at 199—200°. The acetyl derivative crystallises in pale-yellow needles and melts at 120—121°. α-Benzile-

oxime combines with phenylhydrazine on heating in alcoholic acetic acid solution at 40° and forms *benzileoximehydrazone*,

$$OH{\cdot}N{:}CPh{\cdot}CPh{:}N{\cdot}NHPh,$$

which crystallises in colourless needles melting at 172—173°. The γ-oxime does not react with phenylhydrazine under these conditions. The *acetyl derivative* is formed by the action of acetic anhydride on the oximehydrazone at low temperatures; it crystallises in small, lustrous, yellow plates melting at 109°.

On treatment with hydroxylamine, benzilephenylhydrazone yields triphenylisotriazone, $NPh<\begin{matrix}N{:}CPh\\ |\\ N{:}CPh\end{matrix}$, which melts at 120—121°.

J. B. T.

Acids from the Dicyanhydrin of Benzoylacetone. By M. Carlson (*Ber.*, **25**, 2728—2731).—The *dicyanhydrin*,

$$CH_2[CPh(CN){\cdot}OH]_2,$$

obtained by mixing an alcoholic solution of benzoylacetone with potassium cyanide, and gradually adding hydrochloric acid of sp. gr. 1·19, yields, on boiling with dilute hydrochloric acid, two isomeric monobasic lactonic acids, $C_{12}H_{12}O_5$, melting at 174—175° and 163° respectively. The same *methylphenyldihydroxyglutaric acid*, $C_{12}H_{14}O_6$, of melting point 168°, is produced on treating the potassium salts of either of the lactonic acids with the necessary quantity of hydrochloric acid. On heating the dihydroxy-acid at 170—175°, it is converted into a mixture of the two lactonic acids. A. R. L.

Naphthylene Dihydrosulphide and Dithiocyanate. By L. Braun and R. Ebert (*Ber.*, **25**, 2735—2739; compare Abstr., 1891, 460).—Naphthylene dihydrosulphide [$(SH)_2 = 2:3'$] (*loc. cit.*) is obtained in most favourable yield (11·6 per cent. of the theoretical) by heating the corresponding sulphonic chloride with zinc dust and acetic acid over a free flame. On extracting the dihydrosulphide with alcohol, the residue was found to be insoluble in ether, and on further extraction with benzene, it was obtained free from chlorine; it then melted at 270°, and appeared to be a naphthylene bisulphide. When the above-mentioned sulphonic chloride is heated with hydriodic acid and phosphorus for 10 hours, 2·6 per cent. of the theoretical amount of dihydrosulphide was isolated, whilst only naphthalene was obtained on continuing the heating for 24 hours. The pure dihydrosulphide forms colourless, lustrous scales, melts at 177—178°, and has a faint characteristic odour. A dithiocyanate, resembling that already described (*loc. cit.*), but melting at 96°, was obtained by treating the lead compound of the dihydrosulphide, suspended in alcohol, with cyanogen chloride or bromide.

1 : 4'-*Naphthalene dihydrosulphide* passes over in an amount reaching 80 per cent. of the theoretical when the corresponding sulphonic chloride is heated on the water-bath with zinc dust and acetic acid in a current of steam; it forms lustrous, silvery leaflets which become yellowish on keeping, and melts at 103°. A. R. L.

Orthodiamines. By O. Fischer (*Ber.*, **25**, 2826—2846; see also Abstr., 1891, pp. 434, 746, and 1109).—The compounds obtained by the condensation of mono-substituted orthodiamines with aldehydes may be either benzylidene compounds or dihydroimidazoles, and have the constitution $NHR'\cdot C_6H_4\cdot N{:}CHR'$ or $C_6H_4{<}\overset{NH}{NR'}{>}CHR'$. Thus, when boiled with acids they are resolved into their components, and, therefore, behave like benzylidene compounds, and it is probable that such benzylidene compounds on oxidation would yield anhydro-bases. However, ethylamidophenylnaphthylamine, $NHPh\cdot C_{10}H_6\cdot NHEt$, when treated with benzaldehyde, yields a condensation product which is resolved into its components by acids, and cannot be a benzylidene compound and must be regarded as a dihydroimidazole. The author is of opinion that the condensation products from mono-substituted orthodiamines are also dihydroimidazoles.

When orthophenylnaphthylenediamine and benzaldehyde in molecular proportion, mixed with a few drops of absolute alcohol, are warmed at 50—70° for 15—20 minutes, a yellow, crystalline compound is obtained of the formula $NHPh\cdot C_{10}H_6\cdot N{:}CHPh$ or

$$C_{10}H_6{<}\overset{NH}{NPh}{>}CHPh.$$

It crystallises from alcohol or benzene in sulphur-yellow prisms, melts at 138°, is insoluble in water, easily soluble in alcohol, benzene, chloroform, and ether, and by boiling with acids is resolved into benzaldehyde and phenylnaphthylenediamine.

Phenylbenzenyl-αβ-naphthylenediamine, $C_{10}H_6{<}\overset{\quad N}{NPh}{>}CPh$, is obtained by warming the mixture of benzaldehyde and orthophenylnaphthylenediamine for 4—5 hours on the water-bath. It is also obtained by repeated crystallisation of the preceding compound from boiling alcohol. It crystallises in white needles, melts at 142—143°, is not decomposed by boiling with acids, and is somewhat soluble in hot water, sparingly in alcohol and benzene, and easily so in a mixture of the last solvents. The alcoholic solution has a beautiful blue fluorescence. The *hydrochloride* is a crystalline powder, sparingly soluble in water. The *platinochloride* crystallises in yellow leaflets, and is sparingly soluble in alcohol. The *sulphate* crystallises in slender, pale rose-coloured needles.

Salicylaldehyde and orthophenylnapthylenediamine yield a brick-red condensation product which crystallises in red, interlacing needles, melts at 139°, is easily soluble in alcohol, benzene, and ether, and is resolved into its components when boiled with acids.

Phenylhydroxybenzenylnaphthylenediamine is obtained by repeated crystallisation of the preceding red compound; it forms yellowish-white leaflets, melts at 175—176°, and is easily soluble in alcohol, ether, and benzene. The *hydrochloride* is very sparingly soluble in water, and crystallises from alcohol in slender, white needles.

The three nitrobenzaldehydes and orthophenylnaphthylenediamine yield similar condensation products to the above. Brown or

red compounds are first formed and by repeated crystallisation are converted into bright-yellow anhydro-bases.

Phenylorthonitrobenzenylnaphthylenediamine crystallises from alcohol in lemon-yellow, silky needles, melts at 242°, is easily soluble in benzene, and somewhat sparingly so in alcohol. The alcoholic solution has a pale greenish-yellow fluorescence. The *platinochloride* crystallises from alcohol in beautiful golden leaflets.

Phenylparanitrobenzenylnaphthylenediamine crystallises in golden needles, melts at 238°, and is sparingly soluble in alcohol, more easily so in benzene.

Phenylmetanitrobenzenylnaphthylenediamine crystallises from alcohol in yellow tablets and melts at 209°.

Phenylisopropylbenzenylnaphthylenediamine is obtained by repeated crystallisation of the brownish-red condensation product from cuminaldehyde and orthophenylnaphthylenediamine. It crystallises in six-sided leaflets, melts at 136°, and is easily soluble in alcohol, benzene, and ether.

Paratolylorthonaphthylenediamine was prepared by adding paratolyl-β-naphthylamine to an alcoholic solution of diazobenzene chloride and then reducing the azo-derivative with stannous chloride and acetic acid. It crystallises from alcohol or light petroleum in needles or plates, is obtained in very beautiful crystals from methyl alcohol, melts at 128°, and turns violet on exposure to light.

A *thio-compound* of the formula $C_{10}H_6{<}^{NH\ \ ---}_{N(C_7H_7)}{>}C{:}S$ or

$$C_{10}H_6{<}^{\overline{\quad}\ N}_{N(C_7H_7)}{>}C{\cdot}SH$$

is obtained by boiling the preceding diamine with carbon bisulphide for four hours in a reflux apparatus. It crystallises from acetic acid in beautiful pale-yellow needles, melts at 307°, is insoluble in benzene, light petroleum, and chloroform, very sparingly soluble in alcohol, and yields a very unstable sodium salt which crystallises in beautiful lustrous, white leaflets.

The *anhydro-base*, $C_{10}H_6{<}^{\overline{\quad}\ N}_{N(C_7H_7)}{>}CPh$, is obtained by warming molecular proportions of paratolylorthonaphthylenediamine and benzaldehyde mixed with a little absolute alcohol on the water-bath for half an hour. It crystallises from alcohol in beautiful white prisms, melts at 155°, is easily soluble in benzene, petroleum, and ether, more sparingly so in alcohol, and is not decomposed by boiling with dilute sulphuric acid.

With metanitrobenzaldehyde, the above diamine yields a similar anhydro-base, which crystallises from alcohol in aggregates of yellowish-brown needles, and melts at 197°; it is insoluble in water, but soluble in alcohol and benzene, more sparingly so in ether and light petroleum.

Salicylaldehyde and paratolylnaphthylenediamine yield a red crystalline compound which, on recrystallisation, is converted into the *anhydro-base*. The latter crystallises from alcohol in yellowish-green leaflets, melts at 217°, is soluble in benzene, ether, and light petroleum,

and insoluble in water. It dissolves in concentrated sulphuric acid with a blue coloration, which on the addition of water turns red and finally disappears.

Tolyldiphenylnaphthodihydroquinoxaline, $C_{10}H_6<\begin{matrix}N=CPh\\N(C_7H_7)\end{matrix}>CHPh$, is prepared by heating benzoïn and paratolylnaphthylenediamine, in molecular proportion, in a sealed tube at 210° for two hours. It crystallises from absolute alcohol in lustrous, yellow leaflets, melts at 173°, is insoluble in water, very sparingly soluble in alcohol, easily so in ether, benzene, and petroleum; with mineral acids, it gives dark-red salts which are decomposed by water.

The *azonium base*, $C_{10}H_6<\begin{matrix}N=CPh\\N(OH)(C_7H_7)\end{matrix}>CPh$, is obtained by oxidising the preceding compound in alcoholic solution with ferric chloride. It crystallises from absolute alcohol in yellowish-green prisms, and melts at 194°. The solution in ether, benzene, petroleum, or absolute alcohol exhibits a beautiful yellowish-green fluorescence. It dissolves in concentrated sulphuric acid with a dark reddish-violet coloration, which, on the addition of water, successively turns bright red and then pure yellow, with a strong fluorescence. The *iron salt*, $C_{31}H_{23}N_2Cl,FeCl_3$, is soluble in water, insoluble in alcohol, and is decomposed by boiling with sodium carbonate. The *hydrochloride* crystallises from dilute alcohol in lustrous, broad, yellow plates, containing 1 mol. of alcohol, and is sparingly soluble in water. The *hydrobromide* crystallises from dilute alcohol in lustrous, yellow leaflets. The *nitrate* crystallises from dilute alcohol in yellow needles, and is sparingly soluble in water, easily so in alcohol. The *sulphate* crystallises in yellow leaflets The azonium base is also obtained by heating dibenzoyl and tolylnaphthylenediamine, in molecular proportion, in concentrated alcoholic solution until a sample no longer gives a red coloration with ferric chloride. The yield is quantitative.

When orthophenylenediamine hydrochloride is heated with methyl alcohol (4 mols.) for three hours at 180°, and the product treated with sodium hydroxide, distilled with steam, and the distillate extracted with ether, a dark-coloured, viscid oil is obtained which cannot be purified by fractional distillation. If this oil is treated with acetic anhydride and the acetyl compounds mixed with dilute soda and distilled with steam, a yellow oil passes over, and long, slender needles separate from the aqueous liquid on cooling. The needles are methylphenylenethenylamidine. The oil, on fractional distillation, yields a small quantity of tetramethylorthophenylenediamine, boiling at 215—218°.

Tetramethylorthophenylenediamine is easily obtained by heating orthophenylenediamine with methyl iodide and methyl alcohol, at 180°, for 10 hours. It boils at 215—218°, under a pressure of 735 mm., is insoluble in sodium hydroxide, sparingly soluble in water, easily so in most organic solvents; it is extremely sensitive to light and air, and soon turns black on exposure with partial decomposition. The *hydrochloride* crystallises in small, colourless prisms, melts at 180°, is soluble in water in all proportions, less soluble in absolute alcohol, and quickly turns red on exposure to air. The *platinochloride* crystallises in stout, reddish-brown crystals.

Methylphenylenethenylamidine, $C_6H_4<^{NMe}_{\ \ N}>CMe$, is also obtained by heating phenylethenylamidine with methyl iodide in a sealed tube at 100°. It distils at 290°, solidifies in the receiver in radiating needles, and melts at 112°. The *hydrochloride* is obtained in beautiful crystals by adding alcoholic hydrogen chloride to an alcoholic solution of the base, and is extremely soluble in water. The *platinochloride* crystallises in beautiful brown needles. The *aurochloride* crystallises in lustrous, golden needles. The *methiodide* is obtained by heating the base with methyl iodide in a sealed tube at 100°; it crystallises in large prisms, and melts at 254°.

Methylorthophenylenediamine is obtained by methylating orthonitraniline, and, after purifying the methylnitraniline by steam distillation, reducing it with tin and hydrochloric acid. The product is then purified by steam distillation. It boils at 245—248° under 736 mm. pressure, and quickly darkens on exposure to air. The *hydrochloride* separates in well formed rhombic crystals, melts at 191°, and is sensitive to light and air. When the base is boiled with acetic anhydride, it is converted into ethenylmethylphenyleneamidine. When warmed with benzaldehyde, it yields a compound of the formula

$$C_6H_4<^{NMe}_{\ \ N}>CPh.$$

This crystallises from dilute alcohol in slender, colourless needles, and melts at 170—171°. With orthonitrobenzaldehyde, the diamine yields the benzylidene derivative, $NHMe\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4\cdot NO_2$. This crystallises from ether in lustrous, yellow leaflets, and is resolved into its components when boiled with acids. With salicyldehyde, the diamine yields a yellow, crystalline compound, which melts at 110—111°, and is resolved into its components when boiled with acids. By repeated crystallisation from alcohol, it is converted into the anhydro-base. The latter is colourless, and melts at 164—165°.

Difurylquinoxaline, $C_6H_4<^{N=C\cdot C_4OH_3}_{N=C\cdot C_4OH_3}$, is obtained by heating furoïn and orthophenylenediamine in a sealed tube, at 150°, for four hours. It crystallises from alcohol in pale-yellow needles, melts at 134°, and is easily soluble in benzene, ether, and chloroform, but only very sparingly in light petroleum. The solution of the impure product in ether or benzene exhibits a violet-blue fluorescence. An attempt to prepare difuryldihydroquinoxaline by filling the tube with carbonic anhydride was unsuccessful.

Difurylnaphthoquinoxaline is obtained by heating furoïn and $\alpha\beta$-naphthylenediamine at 200°. A small quantity of the dihydro-compound is also obtained, and imparts a greenish-blue fluorescence to the solutions of the crude product. It crystallises from alcohol in golden needles, and melts at 147°.

Difuryltoluquinoxaline, prepared from 1 : 3 : 4-toluylenediamine in the same way, crystallises from alcohol in yellow needles, melts at 176°, and is easily soluble in ether and benzene, sparingly in light petroleum.

Phenyldifurylnaphthodihydroquinoxaline, $C_{26}H_{18}N_2O_2$, is obtained from furoïn and phenylnaphthylenediamine; it crystallises from alcohol

in yellow needles, and melts at 176°. The solution in ether or benzene exhibits a beautiful yellowish-green fluorescence. The *hydrochloride* crystallises in claret coloured needles. When oxidised in alcoholic solution with ferric chloride, it yields the *azonium base*, $C_{10}H_6<\begin{matrix}N = C\cdot C_4OH_3\\ NPh(OH)\end{matrix}$; this crystallises from alcohol in beautiful transparent, yellowish-green prisms, melts at 160°, and is easily soluble in ether, benzene, and chloroform, sparingly in light petroleum.

Tolyldifurylnaphthodihydroquinoxaline is obtained from furoïn and paratolylnaphthylenediamine. It crystallises from alcohol in lustrous, yellow needles, and melts at 186°. The solution in benzene or ether shows a beautiful greenish-yellow fluorescence. The alcoholic solutions of the salts are intensely dark-red.

In the preparation of the preceding compound, *benzeneazo-β-tolylnaphthylamine* and *tolylnaphthylenediamine* were prepared. The former crystallises from acetic acid in lustrous, dark-red leaflets, and melts at 156°. The latter crystallises from petroleum in aggregates of lustrous, white needles, and melts at 146—147°. E. C. R.

Formation of Indulines. By O. Fischer and E. Hepp (*Ber.*, **25**, 2731—2734).—Whereas the formation of indulines from anilidoquinoneimides is readily explained, that of the quinoneimides from amidoazo-compounds is obscure. Assigning a hydrazone formula to amidoazobenzene (Goldschmidt), the formation of anilidoquinonediimide is represented by the following intramolecular change:— $NH{:}C_6H_4{:}N\cdot NHPh = NH{:}C_6H_5(NH)\cdot NHPh$. When benzeneazo-α-phenylnaphthylamine is heated at 130° with 80 per cent. acetic acid, a small quantity of anilidonaphthaquinoneanil is formed; also, when benzeneazo-α-naphthol is boiled for 8—10 hours with glacial acetic acid, a certain quantity of anilidonaphthaquinone (Plimpton, Trans., 1880, 639) is obtained. The primary product in the last case is, doubtless, the anilidoquinoneimide, $O{:}C_{10}H_5(NH)\cdot NHPh$ [1 : 3 : 4]. Besides the quinone derivative and unaltered benzeneazo-α-naphthol, an amorphous compound, $C_{24}H_{19}N_3O_2$, melting at 233° was also isolated; this, when boiled with alcoholic sulphuric acid, gives a compound which is, perhaps, a carbazole derivative. A. R. L.

Action of Aniline on β-Naphtholcarboxylic Acid. By M. Schöpff (*Ber.*, **25**, 2740—2745).—When 2 : 3-naphtholcarboxylic acid (m. p. 216°) is heated with an excess of aniline in a reflux apparatus for 8—10 hours, the product mixed with dilute hydrochloric acid, and the excess of aniline boiled off, the solid portion, after extracting with hot alcohol, consists of *β-hydroxynaphthoic anilide*, $OH\cdot C_{10}H_6\cdot CONHPh$, which crystallises from glacial acetic acid in nacreous leaflets, but is insoluble in most solvents, and melts at 243—244°. On adding water to the alcoholic extract, a precipitate is produced, which is collected, and, on treatment with sodium carbonate solution, leaves *β-anilidonaphthoic anilide*, $NHPh\cdot C_{10}H_6\cdot CONHPh$; this crystallises from glacial acetic acid in greenish tables, and melts at 168—169·5°. *β-Anilidonaphthoic acid*, $NHPh\cdot C_{10}H_6,COOH$, is contained in the sodium carbonate solution together with a large quantity of unaltered naph-

tholcarboxylic acid, and is separated from the latter by fractional precipitation with an acid; it crystallises from alcohol in golden-yellow needles, and melts at 235—237°; the *sodium* salt contains $1\frac{1}{2}$ mols. H_2O. When the acid is heated with zinc chloride at 200—220°, a compound is obtained, dissolving in most solvents with an intensely green fluorescence; it is, probably, *phenonaphthacridone*, $C_{10}H_6<\overset{NH}{CO}>C_6H_4$ (compare this vol., p. 1223), and is being further investigated. A. R. L.

1 : 2-Dicyanonaphthalene and 1 : 2-Naphthalenedicarboxylic Acid. By P. T. Cleve (*Ber.*, **25**, 2475—2479).—1 : 2-*Dicyanonaphthalene* is prepared by heating potassium 1 : 2-chlorosulphonate with dehydrated potassium ferrocyanide in a rapid current of carbonic anhydride. The yield amounts to about 12 per cent. of the potassium salt employed. It crystallises from benzene in flexible, asbestos-like needles, sublimes in long, lustrous, colourless needles, melts at 190°, and dissolves sparingly in alcohol, more readily in chloroform, benzene, acetic acid, or amyl alcohol. By prolonged heating with hydroxylamine, it is converted into the *dioximimide* of naphthalenedicarboxylic acid, $C_{10}H_6<\overset{C(N\cdot OH)}{C(N\cdot OH)}>NH$, a yellowish, crystalline powder, which melts at 260°, is very sparingly soluble in alcohol, benzene, or chloroform, and on treatment with acetic anhydride, yields a crystalline *diacetyl* derivative, $C_{10}H_6{:}C_2N_2(OAc)_2{:}NH$, melting at 213°.

1 : 2-*Naphthalenedicarboxylic acid*, $C_{10}H_6(COOH)_2$, obtained by the hydrolysis of the dicyano-derivative, is a heavy, crystalline powder, sparingly soluble in cold, but tolerably soluble in hot, water. It melts at 175°, undergoing conversion into the *anhydride*, which sublimes in long, colourless needles, melts at 165°, and dissolves readily in benzene, but is almost insoluble in water. The anhydride gradually regenerates the acid on boiling with water, and in many respects resembles phthalic anhydride, giving phthaleïns, for example, when heated with phenol or resorcinol and zinc chloride. *Potassium naphthalenedicarboxylate* is very soluble, and crystallises from a syrupy solution in tabular forms. Acetic acid precipitates from its aqueous solution a sparingly soluble, crystalline salt of the composition $C_{10}H_6(COOH)_2 + COOH\cdot C_{10}H_6\cdot COOK + 4H_2O$. The *sodium* salt is also very soluble, and, from its solution, acetic acid precipitates a sparingly soluble, crystalline, acid sodium salt of analogous composition. The *silver*, *magnesium*, *calcium* with $1H_2O$, *barium*, *barium hydrogen* with $8H_2O$, and *copper* salts are described. The *amide*, $C_{10}H_6(CONH_2)_2$, crystallises in small, rhombic forms, dissolves sparingly in water but readily in aqueous soda, and melts at 265°, evolving ammonia, and undergoing conversion into the *imide*, $C_{10}H_6{:}C_2O_2{:}NH$, which sublimes in long needles, melts at 224°, and is sparingly soluble in benzene and chloroform. W. J. P.

Chloronaphthalenesulphonic Acids. By P. T. Cleve (*Ber.*, **25**, 2479—2484).—After summarising the work of himself and his pupils on the chloronaphthalenesulphonic acids, the author describes a series of salts of the following acids.

1 : 2′-α-Chloronaphthalenesulphonic acid (compare Armstrong and Wynne, Proc., 1889, 49), prepared from 1 : 2′-α-amidonaphthalenesulphonic acid (Abstr., 1889, 155) by Sandmeyer's method, is readily soluble, and crystallises in aggregates of needles. The *potassium*, *barium* with $3H_2O$, and *silver* salts are described. The *ethyl* salt, $C_{10}H_6Cl{\cdot}SO_3Et$, crystallises from alcohol in large, flat plates, and melts at 90°. The chloride melts at 94°, and the amide at 181° (185—186° according to Armstrong and Wynne).

2 : 4′-β-Chloronaphthalenesulphonic acid, obtained from 2 : 4′-β-amidonaphthalenesulphonic acid (Dahl's acid) by Sandmeyer's method (compare Armstrong, *Brit. Assoc. Rep.*, 1888; Armstrong and Wynne, Proc., 1889, 498), crystallises from a concentrated solution in tolerably large, tabular crystals. The *potassium* with H_2O, sodium with H_2O, *calcium* with $2H_2O$, *barium* with $2H_2O$, *zinc* with $6H_2O$, *copper* with $7H_2O$, and *silver* salts are described. The *ethyl* salt, $C_{10}H_6Cl{\cdot}SO_3Et$, crystallises from alcohol in large and somewhat sparingly soluble prisms, and melts at 114·5°. The chloride melts at 69°, the *amide* crystallises in silvery scales melting at 214°.

2 : 2′-Chloronaphthalenesulphonic acid, prepared from 2 : 2′-amidonaphthalenesulphonic acid (F-, or Bayer and Duisberg's acid) by Sandmeyer's method (compare Armstrong, *loc. cit.*; Armstrong and Wynne, Proc., 1889, 49), crystallises with $4H_2O$ from a concentrated solution in large, tabular forms, which melt at 68°; the anhydrous acid melts at 118°. The *potassium* with H_2O, *sodium*, *magnesium* with $8H_2O$, *calcium* with $8H_2O$, *barium* with H_2O, *lead* with $2H_2O$, *zinc* with $8H_2O$, *copper* with $8H_2O$, and *silver* salts are described. The *methyl* salt, $C_{10}H_6Cl{\cdot}SO_3Me$, is obtained from alcoholic solution in well-formed crystals, and melts at 89°; the *ethyl* salt melts at 65°. The chloride melts at 86·5°, and the amide at 176°. W. J. P.

1 : 2 : 2′-α-Nitrochloronaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **25**, 2485—2490).—The chloride of 1 : 2 : 2′-*α-nitrochloronaphthalenesulphonic acid* [$NO_2 : Cl : SO_3H = 1 : 2 : 2'$] is obtained by introducing finely-powdered 2 : 2′-chloronaphthalenesulphonic chloride into cooled nitric acid of sp. gr. 1·5. Accompanying the 1 : 2 : 2′-derivative is a small quantity of a second chloride, which melts at 145°, but has not been further examined. The *potassium*, *sodium*, *calcium* with $5H_2O$, *barium* with $3H_2O$, and *silver* salts of 1 : 2 : 2′-nitrochloronaphthalenesulphonic acid are described. The *ethyl* salt, $NO_2{\cdot}C_{10}H_5Cl{\cdot}SO_3Et$, crystallises in almost colourless, microscopic needles, melts at 184°, and is very sparingly soluble in alcohol or chloroform. The *chloride* forms small, bright yellow needles, melts at 219°, and dissolves very sparingly in acetic acid or chloroform; the *amide* crystallises in slender, pale yellow, asbestos-like needles, and melts at 247°. On treatment with hydriodic acid, the chloride is converted into a sparingly soluble substance of the composition $(C_{10}H_5Cl{\cdot}NO_2)_2S_2$, melting at 217°, and the amide into 1 : 2′-α-amidonaphthalenesulphonamide (Abstr., 1889, 155). On distillation with phosphorus pentachloride, the chloride yields a trichloronaphthalene which crystallises in small, granular forms, melts at 75·5°, dissolves readily in alcohol

and acetic acid, and is regarded as identical with Alén's trichloronaphthalene of like melting point.

1 : 2 : 2'-*α-Amidochloronaphthalenesulphonic acid*, obtained from the potassium salt of the nitro-acid by boiling with ferrous sulphate and aqueous potash, crystallises in microscopic needles, and is tolerably soluble in boiling water. It is converted by Sandmeyer's method into 1 : 2 : 2'-dichloronaphthalenesulphonic acid, and of this acid the *potassium*, *sodium* with H_2O, *silver* with H_2O, *magnesium* with $9H_2O$, *calcium* with $2H_2O$, and *barium* with $3H_2O$ salts are described. The *ethyl* salt, $C_{10}H_5Cl_2{\cdot}SO_3Et$, crystallises from alcohol in small needles, and melts at 123°. The chloride melts at 124°, and the amide at 227° (compare Armstrong and Wynne, Proc., 1889, 49). On hydrolysis, the potassium salt yields 1 : 2-dichloronaphthalene.

W. J. P.

3'-Methyl-α-naphthindole. By A. Reissert and A. Junghahn (*Ber.*, **25**, 2698—2700).—3'-*Methyl-α-naphthindole*, $C_{10}H_6{<}\overset{NH}{CMe}{>}CH$, is prepared by heating α-naphthylamine (2 mols.) with chloracetone (1 mol.) on the water-bath for four hours, and, after extracting the α-naphthylamine hydrochloride from the product with hot water, collecting the residue, drying, powdering, and distilling it. The solid distillate is repeatedly recrystallised from alcohol, when it forms lustrous, silvery plates; it is readily soluble in acetic acid, benzene, and hot alcohol, melts at 198°, and decomposes with the formation of a blue liquid on boiling with concentrated hydrochloric acid; a pine splinter moistened with hydrochloric acid is coloured blue by its solutions. The *acetyl* derivative, $C_{13}H_{10}NAc$, formed by boiling the compound with acetic anhydride, crystallises from alcohol in faint, reddish needles, and melts at 228°. An isomeric methyl-α-naphthindole is described by Schlieper (Abstr., 1887, 964).

A. R. L.

Menthene. By F. A. Sieker and E. Kremers (*Amer. Chem. J.*, **14**, 291—293).—Fifty grams of menthol and 100 grams of potassium hydrogen sulphate are heated in a reflux apparatus for 6—8 hours at a temperature of 180—200°. The product is steam distilled and the resulting oil fractionated, yielding menthene, boiling at 167—168°, and unchanged menthol. Menthene thus obtained is a colourless, mobile liquid, of a peculiar (not menthol-like) odour. Its specific gravity at 20° is 0·814. It is dextrorotatory, $[\alpha]_D = +26{\cdot}40°$, although obtained from lævorotatory menthol.

The nitrosite reaction, as applied by Wallach to terpinene, gave no result with menthene. A *nitrosochloride*, $C_{10}H_{18}NOCl$, was obtained as a white, crystalline powder as follows:—15 c.c. of menthene was dissolved in 15 c.c. of glacial acetic acid and 11 c.c. of ethyl nitrite, and cooled; 6 c.c. of hydrochloric acid in an equal volume of glacial acetic acid was then added gradually. About 4 grams of white, crystalline nitrosochloride was obtained. It was purified by dissolving in the smallest possible quantity of chloroform, filtering, and precipitating with alcohol. It melts at 113° without decomposition, but decomposes at about 152°. It is readily soluble in chloroform, less so in ether, and but sparingly soluble in alcohol.

Menthene nitrosochloride, when heated with benzylamine, yields a crystalline substance, very likely a nitrolamine base. The study of menthene and its derivatives will be continued. W. T.

Cantharene. By J. Piccard (*Ber.*, **25**, 2453).—The author quotes from his previous papers to show that he has long anticipated Baeyer's conclusion (this vol., p. 1183) that cantharene is probably a dihydro-orthoxylene, of the nature of a terpene. C. F. B.

Cineolic Acid. By G. Elkeles (*Annalen*, **271**, 20—27).—*Cineolic piperidide*, $COOH\cdot C_8H_{14}O\cdot CO\cdot C_5NH_{10}$, is obtained in colourless crystals when a dry ethereal solution of cineolic anhydride is treated with anhydrous piperidine in molecular proportion, and then evaporated in a dry atmosphere; it melts at 151—152°, and forms a sparingly soluble *silver* salt of the composition $COOAg\cdot C_8H_{14}\cdot OCO\cdot C_5NH_{10}$. The *allylamide*, $COOH\cdot C_8H_{14}O\cdot CO\cdot NH\cdot C_3H_5$, prepared in like manner, separates from a mixture of ether and methyl alcohol in crystals, and melts at 126°. The *diethylamide*, $COOH\cdot C_8H_{14}O\cdot CO\cdot NEt_2$, is a colourless, crystalline compound, melting at 162—163°. The *anilide* is a syrup, but when treated with anhydrous ammonia in ethereal solution, it is converted into a solid, colourless, hygroscopic *ammonium* salt, from which the *silver* salt, $COOAg\cdot C_8H_{14}O\cdot CO\cdot NHPh$, can be prepared; the last-named compound reacts with methyl iodide, yielding the *methyl* salt, $COOMe\cdot C_8H_{14}O\cdot CO\cdot NHPh$, a crystalline compound melting at 78—79°. The *paratoluidide*,

$$COOH\cdot C_8H_{14}O\cdot CO\cdot NH\cdot C_6H_4Me,$$

separates from a mixture of ether and methyl alcohol in crystals melting at 125—126°; its *silver* salt, $COOAg\cdot C_8H_{14}O\cdot CO\cdot NH\cdot C_6H_4Me$, is a colourless, amorphous compound. The *phenylhydrazide*,

$$COOH\cdot C_8H_{14}O\cdot CO\cdot N_2H_2Ph,$$

crystallises in needles, and melts at 110°. The *amide*,

$$COOH\cdot C_8H_{14}O\cdot CO\cdot NH_2,$$

is crystalline.

When the paratoluidide described above is submitted to dry distillation, it is decomposed into toluidine, carbonic oxide, carbonic anhydride, and the compound of the composition $C_8H_{14}O$, previously described by Wallach (Abstr., 1890, 1314); the last-named substance is slowly converted into metaxylene when boiled with dilute sulphuric acid, more quickly when heated with the dilute acid at 150°.

The monocarboxylic acid, $C_8H_{15}O\cdot COOH$, obtained by heating cineolic acid (compare Wallach, *loc. cit.*) can be converted into its methyl salt by treating it with hydrogen chloride in methyl alcoholic solution; this compound boils at 125°, under a pressure of 13 mm., and has the composition $C_{10}H_{18}O_3$. F. S. K.

Kuromoji Oil. By W. Kwasnik (*Arch. Pharm.*, **230**, 265—286).—The volatile oil is obtained from the "Kuromoji" (*Lindera sericea*, Blume), a tree growing in all the uplands of Japan, and appears to be derived from both the wood and the leaves of the

plant. It was only introduced into Europe in 1888, and has not hitherto been chemically investigated. The material examined was obtained from Schimmel, of Leipsic. It is clear, dark-yellow in colour, has a strong aromatic odour, and a sp. gr. of 0·901 at 18°, 0·896 at 20°. It is very feebly lævorotatory, the small amount of the rotation being due to the presence of nearly equal quantities of dextro- and lævo-rotatory constituents. It forms a clear solution in alcohol, ether, benzene, light petroleum, acetic acid, and fatty oils. In chloroform and carbon bisulphide, it forms a cloudy solution, but the solution in chloroform is rendered clear by the addition of a small quantity of alcohol. It contains neither nitrogen nor sulphur, and is neutral to litmus. It is attacked by metallic potassium in the cold, gives a dark, somewhat violet coloration with ferric chloride, and decolorises potassium permanganate in the cold. Its constituents were partially separated by repeated fractional distillation, and isolated and identified by chemical means. The oil was thus found to contain: (1) dextrorotatory limonene, $C_{10}H_{16}$; (2) dipentene, $C_{10}H_{16}$; (3) terpineole, $C_{10}H_{18}O$; and (4) carvol, $C_{10}H_{14}O$, all of which are nearly related to one another, and for the most part interconvertible.

C. F. B.

Camphene and Camphoric Acid. By O. Wallach (*Ber.*, **25**, 2444).—The author declines to again correct the misstatements in a recently published paper of Brühl's (this vol., p. 1240).

Hydrazones of Camphoric Acid. By E. M. Chaplin (*Ber.*, **25**, 2565—2568).—Campherylphenylhydrazine is prepared by heating phenylhydrazine and camphoric anhydride in molecular proportion for several hours at 150°, and is identical with the substance obtained by Haller from methyl camphorate and phenylhydrazine; on treatment with alkalis and subsequent acidification, an acid is formed; it has the formula $C_{16}H_{24}N_2O_4$, and is deposited from chloroform in colourless crystals melting at 91—92°; it readily reduces alkaline copper solution.

Acetylcampherylphenylhydrazine $C_{16}H_{19}N_2O_2Ac$, is obtained on heating the hydrazine with 2·5 parts of acetic anhydride, and crystallises from alcohol in prisms which melt at 107°. The *nitro*-derivative, $C_{16}H_{19}N_3O_4$, is prepared by the action of nitrous acid on the hydrazine in acetic acid solution at 0° and crystallises from alcohol in pale-yellow needles melting at 157°. The *dinitro*-derivative, $C_{16}H_{18}N_4O_6$, is formed by the action of nitrous acid on the hydrazine at higher temperatures; it resembles the preceding compound in appearance, is sparingly soluble in alcohol, and melts at 192°.

Paratolylhydrazinecamphoric acid, $C_6H_4Me{\cdot}N_2H_2{\cdot}CO{\cdot}C_8H_{14}{\cdot}COOH$, is prepared by heating paratolylhydrazine with camphoric anhydride at 130°; it crystallises from alcohol in prismatic plates and melts at 193°; when heated at 200°, it yields *campherylparatolylhydrazine*, which is also formed by heating camphoric acid and paratolylhydrazine at 150°; this closely resembles the phenyl derivative in properties, and crystallises in colourless needles melting at 146°.

J. B. T.

Spontaneous Conversion of Isoprene into Caoutchouc. By W. A. Tilden (*Chem. News*, **65**, 265).—The author observed that some isoprene, prepared from turpentine, and stored in bottles, changed spontaneously into india-rubber, the liquid being at the same time acid, and still containing some unchanged isoprene. As an explanation of the phenomenon, it is suggested that the change may be due to the presence of a little acetic or formic acid produced by atmospheric oxidation. D. A. L.

Digitalin. By H. Kiliani (*Arch. Pharm.*, **230**, 250—261; compare also Abstr., 1890, 996; 1891, 576; and this vol., 501).—The leaves and seeds of *Digitalis purpurea* contain *digitonin*, a crystalline inactive glucoside resembling saponin, the crystalline substance *digitoxin*, and two amorphous glucosides, *digitalin* and *digitaleïn*. Of these, digitonin is useless as a remedy for heart disease, and, moreover, causes severe local inflammation, whilst digitoxin is unsuitable as a drug on account of its complete insolubility in water. The other two would be suitable if prepared pure. The digitaleïn of Schmiedeberg is a mixture; not so, however, his digitalin, which is a chemical compound, and is now prepared pure, according to the author's directions, by Boehringer, of Waldhof, and sold under the name of "*Digitalin verum*." This drug is perfectly uniform in its operation, gradually producing cessation of the heart's action, but no injurious secondary effects. Other preparations, such as "*Digitalinum crystallisatum*" and "*D. pur. pulv.*," are impure, and consequently irregular and often injurious in their action. The first of these, indeed, is nearly pure digitonin.

"*Digitalin verum*" is an amorphous, white powder, which is insoluble in chloroform and in ether, swells up in water, and dissolves in it to the extent of 1 part in 1000. 50 per cent. alcohol dissolves 1 part in 100, absolute alcohol still more. The pure substance has but a feebly bitter taste. As tests for its purity, the following may be used:—(1) a few particles placed in a test-tube with 2 c.c. of 10 per cent. aqueous potash should remain white for at least one minute; presence of the other amorphous glucosides causes an immediate yellow coloration. (2) It is stirred with water to a thin paste, 22 parts of amyl alcohol added, with shaking, for every 100 of water used, and the whole allowed to remain in a corked flask; if digitonin is present, it separates out within 24 hours in small, crystalline agglomerates. When heated with strong hydrochloric acid, best with the addition of 50 per cent. alcohol, digitalin is converted into *digitaligenin*, $C_{16}H_{22}O_2$, dextrose, and *digitalose*, $C_7H_{14}O_5$, a sugar which could not be obtained crystalline, but which, when oxidised with bromine, yields *digitalonic lactone*, $C_7H_{12}O_5$. This substance crystallises in fine, colourless prisms, easily soluble in water and alcohol, sparingly in ether. It begins to liquefy at 130°, and melts completely at 138—139°. If it is heated with aqueous soda, and the diluted solution treated with silver nitrate, silver digitalonate, $C_7H_{13}O_6Ag$, crystallises out in tiny needles. C. F. B.

Preparation of Digitogenin. By H. Kiliani (*Arch. Pharm.*, **230**, 261—262).—The method previously given should be modified by carrying out the hydrolysis in alcoholic solution. Digitonin, $C_{27}H_{46}O_{14} + 5H_2O$ (1 part), is heated with 93 per cent. alcohol (8 parts) and concentrated hydrochloric acid of sp. gr. 1·19 (2 parts) for $1\frac{1}{2}$ hours in a reflux apparatus on the water-bath, and the mixture allowed to cool slowly. The digitogenin which separates out, to the extent of about 25 per cent. of the digitonin employed, is removed, the filtrate saturated with chalk, the greater part of the alcohol distilled off, and the residue diluted with water and shaken out with chloroform. The chloroform extract is dried with sodium sulphate, the chloroform distilled off, and the residue crystallised from 93 per cent. alcohol; by this means a further yield of 5 per cent. of digitogenin is obtained. C. F. B.

Cascarin. By Leprince (*Compt rend.*, **115**, 286—288).—*Cascarin*, $C_{12}H_{10}O_5$, is an orange-yellow, crystalline substance obtained from the bark of *Rhamnus prushiana* (*Cascara sagrada*).

An infusion of the dry, powdered bark in boiling, dilute, aqueous sodium carbonate is treated with dilute sulphuric acid to precipitate impurities, and evaporated to dryness, preferably in a vacuum. The residue, after further drying at 60°, is extracted with acetone, the extract treated with sulphuric acid, and, after some time, the solution is poured into a large quantity of warm water. After 24 hours, a greenish-brown deposit settles, and this, on repetition of the treatment, yields cascarin.

Cascarin crystallises in prismatic needles, and is odourless and tasteless. It is insoluble in water, sparingly soluble in chloroform, and easily in alcohol, alcohol-ether, and alkalis, forming purple-red solutions with the last named. It chars at 200°, and melts with decomposition at 300°. When fused with potash, it yields phloroglucol. Jn. W.

Tetravinylpyridine. By G. Karau (*Ber.*, **25**, 2776—2777).—From the fraction 275—290° obtained in the preparation of γ-ethylpyridine, the author has isolated a *tetravinylpyridine*, $C_5NH(C_2H_3)_4$. It is a pale yellow oil boiling at 276—278°; its sp. gr. is 1·0515 at 0°. The *platinochloride* forms orange-yellow, silky needles, sparingly soluble in water, and melting at 175°; the *aurochloride*, pale yellow needles melting at 148°; the *mercurochloride*, long, white, glistening needles melting at 146°. L. T. T.

Piperidine Compounds. By R. Varet (*Compt. rend.*, **115**, 335—337; compare Abstr., 1891, 732 and 838).—*Piperidine argento-iodide*, C_5NH_{11},AgI, is made by heating piperidine with silver iodide in a reflux apparatus at 100° until the iodide has dissolved. The liquid is filtered, and, while still warm, deposits the argento-iodide in slender, transparent needles. Piperidine argento-iodide is blackened by air and light, and is decomposed into its proximate constituents by heat in the absence of light. It is also decomposed by water. *Piperidine argento-bromide*, $2C_5NH_{11},AgBr$, is prepared in the same way at 80°. It crystallises in needles, and is decomposed by water. It

is much more stable than the corresponding pyridine compound (*loc. cit.*). *Piperidine argento-chloride*, $2C_5NH_{11},AgCl$, obtained in the same way, crystallises in prismatic needles, is decomposed by water, and is blackened by light. It is unstable in the presence of air. *Piperidine argento-cyanide*, $2C_5NH_{11},AgCN$, is also made as above. It crystallises in transparent needles, is unstable in presence of air and light, and, when heated, gives off piperidine and cyanogen, the silver being left behind in mirror form. Jn. W.

Oxidation of Piperidine by Hydrogen Peroxide. By R. Wolffenstein (*Ber.*, **25**, 2777—2785).—When pyridine is treated with double the quantity of hydrogen peroxide in 3 per cent. solution, it quickly becomes neutral and then acid, and leaves, on evaporation, a syrup smelling of fatty acids. If the residue is extracted with chloroform, and the extract evaporated and boiled with baryta-water, piperidine and ammonia are evolved, leaving a residue of barium glutarate. The formation of the latter by the oxidation of piperidine may be readily understood; the imido-group is eliminated, and the two methylene groups previously combined with it are oxidised to carboxyl. The portion insoluble in chloroform also consists chiefly of glutaric acid. If the chloroform extract is distilled, it undergoes decomposition, the chief portion passing over at 270°, and becoming solid on cooling; it crystallises from alcohol in lustrous tablets, and consists of *glutarimide*, $CH_2<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>NH$, the manner of formation of which is also manifest; it is a true derivative of piperidine, and has poisonous properties. There is also obtained in the distillation a small quantity of oil which shows the pyrroline reaction, and may be a methylpyrrolidine.

If piperidine is treated with a quantity of hydrogen peroxide sufficient only to add 1 atom of oxygen to the molecule, the product, after 24 hours, no longer smells of piperidine, but has a slightly basic reaction and strongly reducing properties. It is purified by distillation in a current of superheated steam, conversion into the platinochloride and then by the action of hydrogen sulphide into the hydrochloride, which has the composition $C_5H_{12}NOCl$, and gives all the characteristic reactions of an aldehyde. It must therefore be the hydrochloride of *δ-amidovaleraldehyde*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$, the piperidine ring having been split between the imido- and one of the methylene groups, and the latter oxidised to the aldehyde group. The free amidovaleraldehyde is obtained by the action of potassium carbonate on the salts, and on evaporating the ethereal solution crystallises in white plates; it melts at 39°, and is exceedingly soluble in water and light petroleum; the *hydrochloride* crystallises from acetone in monosymmetric crystals, the *hydrobromide* melts at 130°, and the *hydriodide* is a syrup. When the base is heated alone or with solid potash, it loses the elements of water, forming *tetrahydropyridine*. The latter is a strong base which absorbs carbonic anhydride from the air, has an odour intermediate between that of pyridine and piperidine, and, on distillation, undergoes gradual decomposition; its *aurochloride*, $C_5H_9N,HAuCl_4$, is microcrystalline, melts at 141°, and is fairly

soluble in water and alcohol; the *platinochloride* forms small, thick prisms, and the *hydrochloride* and *hydrobromide* melt at 230° and 178° respectively, both previously undergoing decomposition.

Nicotine, as already shown by Pinner and the author (this vol., p. 1010), when treated with hydrogen peroxide, also yields an acid containing an additional atom of oxygen; it has strongly reducing properties, and, on heating, loses water, forming dehydronicotine. The above reactions therefore form additional evidence in favour of the presence of the piperidine ring in nicotine.

If piperidine is mixed with an equal weight of hydrogen peroxide, and allowed to remain for some time, crystals separate, having the composition C_5H_9NO, and melting at 129°; the molecular weight agrees with the above formula, and the substance does not form a nitroso-derivative, but gives the violet phenol reaction with ferric chloride, and must therefore be an *α-hydroxypiperidine*, $CH_2<\begin{matrix}CH_2\cdot C(OH)\\CH_2-\!-CH_2\end{matrix}>N$. It is isomeric with Schotten's piperidone, $CH_2<\begin{matrix}CH_2\text{–}CO\\CH_2\cdot CH_2\end{matrix}>NH$, and may also be obtained by oxidising amidovaleraldehyde with cupric acetate.

Ozone acts on piperidine in the same manner as hydrogen peroxide, but is less active. Pyridine is only attacked with difficulty by hydrogen peroxide, and yields formic acid simply. H. G. C.

Nipecotinic Acid. By A. Ladenburg (*Ber.*, **25**, 2768—2772).—*Nipecotinic acid*, $COOH\cdot C_5NH_{10}$, obtained from the hydrochloride (Abstr., 1891, 735), yields hard, white, and highly refractive crystals. It is exceedingly soluble in water, sparingly so in methyl alcohol, and insoluble in alcohol or ether. It melts at 249—250°. It only shows decided acid characters when in concentrated solutions, and an amorphous deliquescent *sodium* salt was the only salt which could be obtained. On the other hand, as a base it forms a series of crystalline double salts. The *platinochloride* yields orange-red prisms melting at 212—213° (corr.); the *aurochloride* golden-yellow needles melting at 197° (corr.); the double salt with mercuric chloride,

$$C_6H_{11}NO_2,HCl,5HgCl_2,$$

is crystalline, and melts at 229—231°, but begins to decompose at 100°; the *bismuthoiodide* forms ruby-red crystals. That this acid is a secondary amine is shown by the formation of a *nitroso*-derivative, $COOH\cdot C_5NH_9\cdot NO$, which crystallises in prisms, and melts at 111—112°. When the sodium salt is heated with methyl iodide (1 mol.) at 100°, and the product obtained is treated with silver chloride, *methyl nipecotinate hydrochloride*, $COOMe\cdot C_5NH_{10},HCl$, is formed. It is soluble in alcohol and ether, crystallises in needles, and melts at 215—217°. The *platinochloride* crystallises in plates melting at 207—208°. If excess of methyl iodide is employed, a *dimethyl hydrochloride* (*methyl ν-methylnipecotinate hydrochloride*) is obtained as a syrupy mass, which yields a crystalline *platinochloride*, melting at 233—235°. This is probably identical with the platino-salt obtained by Jahn from dihydroarecoline (this vol., p. 739).

L. T. T.

Isonipecotinic Acid. By A. Ladenburg and G. Karau (*Ber.*, **25**, 2772—2775).—Isonicotinic acid, obtained by the oxidation of γ-ethylpyridine, is reduced by means of sodium and amyl alcohol, and the acid formed is purified by conversion into the nitrosamine, which, after crystallisation, is reconverted into the acid. *Isonipecotinic acid*, $COOH{\cdot}C_5NH_{10}$, is easily soluble in water, insoluble in absolute alcohol, crystallises in needles, and remains solid at 320°, although it begins to blacken at 300°. Its concentrated aqueous solution has a slightly acid reaction. The *nitroso*-derivative crystallises in glistening, white needles, melts at 101°, and decomposes at 110°; it is easily soluble in water and alcohol, sparingly in ether. The *hydrochloride* crystallises in long, transparent prisms, soluble in water, sparingly so in absolute alcohol, and melts with decomposition at 228°. Its crystals belong to the rhombic system, giving the axial measurements $a : b : c = 0{\cdot}9217 : 1 : 0{\cdot}9787$. The *hydrobromide* and *hydriodide* form small, white needles, soluble in water and dilute alcohol. The *platinochloride* crystallises in small, yellow prisms, blackens at 230°, and melts at 239°. No well characterised metallic salts could be obtained, the alkaline salts being exceedingly deliquescent. L. T. T.

Piperidinecarboxylic Acids. By A. Ladenburg (*Ber.*, **25**, 2768—2775).—The three theoretically possible piperidinecarboxylic acids having now been prepared, namely, pipecolinic, nipecotinic, and isonipecotinic acids (see two preceding abstracts, and this vol., p. 735), it is found that none of them are identical with the two natural acids, hygric acid (Abstr., 1891, 586), and Zucco's acid from chrysanthemine. Whether these two natural acids are true piperidinecarboxylic acids, are true isomerides, and if so, what the character of their isomerism is, cannot yet be determined. L. T. T.

Phenyllutidinedicarboxylic Acid and Phenyllupetidinedicarboxylic Acid. By L. Kirchner (*Ber.*, **25**, 2786—2791).—*Phenyllutidinedicarboxylic acid*, $C_5NMe_2Ph(COOH)_2$, is obtained from Schiff and Puliti's ethyl hydrophenyllutidinedicarboxylate by oxidising it with nitrous acid, treating the product with sodium carbonate, and hydrolysing the ethyl salt thus obtained. The acid separates from the alkaline solution on the addition of an acid, as a pale-yellow sandy precipitate, which, when slowly crystallised from aqueous solution, forms fern-like aggregates of long, flat needles, and melts at 280° with decomposition. The *hydrochloride*, $C_5NMe_2Ph(COOH)_2,HCl$, forms slender, white needles, and is very unstable; the *mercurochloride* crystallises in small, transparent, pointed needles, blackens at 250°, and melts at 261°. The *copper* salt forms a bluish-green, amorphous precipitate, and the *silver* salt crystallises in small, transparent needles, which are very susceptible to the action of light, and blacken at 215°; the *barium* and *calcium* salts are much more stable, and both crystallise with 7 mols. H_2O. The *dimethyl* salt, $C_5NMe_2Ph(COOMe)_2$, crystallises in extremely slender needles or scales, is insoluble in water, and melts at 139—140°; its *aurochloride*, $C_5NMe_2Ph(COOMe)_2,HAuCl_4$, forms yellow, sparingly soluble needles, and melts with decomposition at 151°.

To convert the acid into the hexahydro-derivative, it is treated with sodium in amyl alcohol solution, and the reduced compound separated from unaltered acid by conversion into the *nitroso-compound*, which forms thick, white needles, melting with decomposition at 190°; it is reconverted into phenyllupetidinedicarboxylic acid by the action of hydrogen chloride, the excess of the latter causing the formation of the *hydrochloride*, $C_5NH_6Me_2Ph(COOH)_2,HCl + H_2O$, which crystallises from hydrochloric acid in small, lustrous needles, becomes brown at 275°, and decomposes completely at 280°. The free *phenyllupetidinedicarboxylic acid*, $C_5NH_6Me_2Ph(COOH)_2$, could not be isolated, as it so readily undergoes decomposition; its *aurochloride* and *mercurochloride* are oils; the *copper* and *silver* salts amorphous precipitates, and the *mercury* salt,

$$C_5NH_6Me_2Ph(COO)_2Hg,$$

a crystalline compound melting at 136°. The alkyl salts cannot be prepared by passing hydrogen chloride into an alcoholic solution of the hydrochloride, but the sodium salt, when heated with an excess of methyl iodide, yields the *methiodide* of the *dimethyl salt* as a thick, pale-yellow oil, which, on treatment with silver chloride, forms the corresponding *methochloride*, $C_5NH_6Me_2Ph(COOMe)_2,MeCl$, the *platinochloride* and *aurochloride* of which are amorphous, insoluble compounds, the latter having the melting point 68°. The *ethiodide* of the *diethyl salt* and the corresponding *ethochloride* are obtained in a similar manner; the latter forms an *aurochloride*, which crystallises in small hard cubes, sinters at 157°, and melts at 164°, and a *platinochloride* which forms crystalline nodules, melts at 165°, and decomposes at 180°. H. G. C.

Dimethyldipiperidyl. By A. Ladenburg (*Ber.*, **25**, 2792—2794). —When 1-methylpiperidine is treated with ethylene bromide, first at 0°, and finally at 250°, for two hours, it behaves in a similar manner to piperidine (*Ber.*, **4**, 738), and is converted into a derivative of dipiperidyl. After removing unaltered ethylene bromide, the product is made alkaline, and distilled in a current of steam, the unaltered methylpiperidine passing over first, and then the less volatile product of the reaction. After purification, the latter forms a liquid boiling at 265° (corr.), which from the analysis and vapour density has the formula $C_{12}H_{24}N_2$, and must therefore be a *dimethyldipiperidyl*. It unites with the moisture of the air, forming a hydrate crystallising in cube-like crystals, the water being again given off in dry air. The *hydrochloride*, $C_{12}H_{24}N_2,2HCl$, forms colourless crystals, stable in the air; the *platinochloride* separates in reddish-yellow plates, even from very dilute solutions, and melts at 236°, previously becoming dark; the *aurochloride*, *mercurochloride*, and *picrate* are also crystalline compounds.

An attempt was made to eliminate the methyl groups, and thus convert the compound into dipiperidyl; the elimination proceeds with considerable difficulty, the chief product of the reaction being piperidine. H. G. C.

Ketones of the Quinoline Series. By L. Berend and E. Thomas (*Ber.*, **25**, 2548—2549).—The authors endeavoured to obtain paracetylquinoline from paramidoacetophenone by Skraup's method, but without success, probably because at the temperature of the reaction the sulphuric acid acts both as a sulphonating and as an oxidising agent; by Doebner's method, however, a satisfactory yield of *paracetylquinaldine*, $C_{10}NH_8Ac$, may be obtained; it crystallises in delicate, silky needles, melts at 92°, and boils without decomposition at 312—320° (uncorr.). The *platinochloride*, $(C_{12}NH_{11}O)_2,H_2PtCl_6 + 3H_2O$, forms yellow, prismatic needles, readily soluble in hot water, and the *picrate*, $C_{12}NH_{11}O,C_6H_3N_3O_7$, forms similar crystals melting at 208—211°. Paracetylquinaldine also combines with phenylhydrazine to form the *hydrazone*, which crystallises from dilute alcohol in reddish-yellow, prismatic needles, and melts at 193°. H. G. C.

Amidoquinolines. By J. Ephraim (*Ber.*, **25**, 2706—2710; compare Abstr., 1891, 1509).—2′-*Phenylhydrazolepidine*,

$$C_9NH_5Me{\cdot}N_2H_2Ph,$$

obtained by heating 2′-chlorolepidine with phenylhydrazine (2 mols.), crystallises from alcohol in white needles, and melts at 197°; when dissolved in glacial acetic acid and oxidised with ferric chloride, it yields the *azo*-derivative, $C_9NH_5Me{\cdot}N_2Ph$, which forms orange-red needles, and melts at 98°. When the hydrazo-compound is boiled with hydriodic acid and amorphous phosphorus for an hour, it decomposes into aniline and Klotz's α-amidolepidine (Abstr., 1888, 1113). 2′-Chlorolepidine does not react with carbamide, but when heated with anthranilic acid, a basic compound, $C_{17}H_{12}N_2O$, is obtained, forming a picrate melting at 217°.

β-Naphthachloroquinaldine, $C_{10}H_6<\begin{matrix}N{-}CMe\\ CCl{:}CH\end{matrix}$, prepared by heating Knorr's β-naphthahydroxyquinaldine with phosphorus oxychloride (2 parts), melts at 159°. When the chloro-compound is heated with aniline (2 mols.), it yields the *anilide*, $C_{13}NH_7Me{\cdot}NHPh$, which crystallises from alcohol in white needles, and melts at 168°; if heated with an equal weight of phenylhydrazine, the *hydrazo*-derivative, $C_{13}NH_7Me{\cdot}N_2H_2Ph$, which forms yellowish-white crystals, and melts at 189°, is obtained. 1′-Chloro-3′-phenylisoquinoline, when heated with aniline, yields the *anilido*-compound, $C_9NH_5Ph{\cdot}NHPh$, melting at 126°, and the *phenylhydrazo*-derivative, $C_9NH_5Ph{\cdot}N_2H_2Ph$, melting at 185°, when heated at 140° with phenylhydrazine. A. R. L.

Alkyl and Alkylene Derivatives of Cinchonic Acid and Alkylene Derivatives of Cinchoxinic Acid. By A. Claus (*Annalen*, **270**, 335—359; compare this vol., p. 1249).—The betaïne of benzylquinoline-γ-carboxylic acid (not β-carboxylic acid, as given by Claus and Muchall, Abstr., 1885, 560) forms monosymmetric crystals, $a : b : c = 0{\cdot}9185 : 1 : 1{\cdot}3413$, $\beta = 95° 41'$, and has the composition $C_{10}H_6NO_2{\cdot}C_7H_7 + 3H_2O$; it separates from glacial acetic acid in yellow, seemingly asymmetric crystals, which retain some of the solvent, and melt at 71°; on oxidation with potassium permanganate,

it yields benzoic acid, benzoylorthamidobenzoic acid and other products.

Benzylidenecinchonic acid, $COOH{\cdot}C_9H_6N{:}CHPh$, is formed when the betaïne is treated with dilute potash and the solution acidified with dilute hydrochloric acid; it crystallises from ether in dark yellow needles, and melts at 218°. It undergoes oxidation so very readily on exposure to the air, that even on recrystallisation from ether it is partially converted into a red, resinous substance; when the residue obtained by evaporating its ethereal solution is treated with soda, the coloured, resinous products readily pass into solution, and benzylidenecinchoxinic acid remains undissolved.

Benzylidenecinchoxinic acid, $O<\begin{matrix}CHPh{\cdot}N{:}C_9H_6{\cdot}COOH\\ |\\ CHPh{\cdot}N{:}C_9H_6{\cdot}COOH\end{matrix}$, purified by means of its barium salt, separates from glacial acetic acid in colourless, lustrous needles, and from chloroform in yellow, well-defined, monosymmetric efflorescent crystals, $a : b : c = 1{\cdot}5993 : 1 : ?$, $\beta = 111° 7'$. It melts at 220°, and dissolves freely in alcohol, ether, chloroform, acetone, and glacial acetic acid, but is insoluble in boiling water; on oxidation with nitric acid of sp. gr. 1·1, it yields terephthalic acid. Its alkali salts are very readily soluble in water, and separate from alcoholic ether in colourless needles. The *barium* salt, $C_{34}H_{24}N_2O_5Ba + 3H_2O$, crystallises in colourless needles, and is only moderately easily soluble in cold water, insoluble in alcohol. The *calcium* salt, $C_{34}H_{24}N_2O_5 + 4H_2O$, crystallises from hot water in flat, nacreous needles. The *silver* salt, $C_{34}H_{24}N_2O_5Ag_2$, crystallises in flat needles, and is stable in the light. The *ethyl* salt, $C_{34}H_{24}N_2O_5Et_2$, prepared by passing hydrogen chloride into an alcoholic solution of the acid, crystallises from ether in lustrous needles, and melts at 120°.

Cinchonic acid ethobromide, $C_{10}H_7NO_2,EtBr$, prepared by heating cinchonic acid with ethyl bromide at 140°, crystallises from alcoholic ether in colourless needles, melts at 237°, and is very readily soluble in water, from which it separates in large, prismatic, efflorescent crystals. The *methiodide*, $C_{10}H_7NO_2,MeI$, crystallises from water in large, red needles, melts at 224°, and is only very sparingly soluble in chloroform, and almost insoluble in ether. The *methochloride*, $C_{10}H_7NO_2,MeCl$, is readily soluble in alcohol, and moderately easily in water, from which it separates in large, yellow, prismatic crystals melting at 243°. The *methobromide* is more sparingly soluble in cold water, crystallises in lustrous, colourless needles, and melts at 262°.

Cinchonic acid methylbetaïne, $C_{11}H_9NO_2$, is easily obtained by treating the methyl halogen compound, with silver oxide, in cold aqueous solution. It crystallises from hot alcohol in slender, lustrous needles, begins to sinter at 180°, melts at 236° with decomposition, and is insoluble in ether and chloroform, but very readily soluble in water; it has an intensely bitter taste, and, with ferric chloride, its aqueous solution gives a red coloration on warming.

Methylenecinchonic acid, $CH_2{:}C_9NH_6{\cdot}COOH$, is best obtained by treating a concentrated solution of the preceding compound with concentrated potash in the cold, covering the mixture with ether, and then acidifying with hydrochloric acid; the solution should be kept cold,

and agitated as little as possible to prevent the oxidation of the acid; on evaporating the dried ethereal solution under reduced pressure, the acid is deposited in brownish-yellow needles, mixed, however, with colourless crystals of methylenecinchoxinic acid. It crystallises in yellow needles, melts at 210°, dissolves freely in alcohol and ether, and very readily undergoes oxidation; on exposure to the air, the crystals turn dark brown or blue, and if, after some time, they are treated with ether, the coloured portions dissolve, leaving colourless crystals of methylenecinchoxinic acid; by evaporating the brown ethereal solution of the intermediate oxidation products, and submitting the residue to the same series of operations, the whole of the methylenecinchonic acid can be transformed into methylenecinchoxinic acid.

Methylenecinchoxinic acid, $O<\begin{matrix}CH_2\cdot N{:}C_9H_6\cdot COOH\\ CH_2\cdot N{:}C_9N_6\cdot COOH\end{matrix}$, can also be obtained by boiling the preceding compound with water in presence of air; it crystallises from hot alcohol and glacial acetic acid in lustrous needles, melts at 249°, and is insoluble in ether and chloroform, and only very sparingly soluble in cold water, but readily in boiling water; it sublimes without decomposition. The *sodium* salt, $C_{22}H_{16}N_2O_5Na_2 + 10H_2O$, is readily soluble in water and alcohol, and separates from water in long, yellow, transparent, efflorescent prisms. The *potassium* salt, $C_{22}H_{16}N_2O_5K_2 + 3H_2O$, crystallises in small needles, and is readily soluble in water and alcohol. The *silver* salt, $C_{22}H_{16}N_2O_5Ag_2$, is a colourless, crystalline compound, insoluble in water.

Cinchonic acid ethiodide, $C_{10}H_7NO_2,EtI$, crystallises from alcohol in orange-yellow needles, melts at about 200° with decomposition, and is soluble in water.

Cinchonic acid ethylbetaïne, $C_{12}H_{11}NO_2 + 2H_2O$, prepared by treating the ethiodide with silver oxide in cold aqueous solution, separates from water in lustrous, colourless crystals which melt at 90—92°, and lose their water at 110°, the anhydrous substance melting at 199° with decomposition; it is readily soluble in water and alcohol, its aqueous solution having a bitter taste, and giving, with ferric chloride, an intense red coloration on warming.

Ethylidenecinchonic acid, $CHMe{:}C_9NH_6\cdot COOH$, is formed when the preceding compound is treated with potash, and is isolated as described in the case of the homologue. It crystallises from ether in brownish-yellow, transparent prisms, and readily undergoes oxidation on exposure to the air in a moist condition. The *silver* salt has the composition $C_{12}H_{10}NO_2Ag$.

Ethylidenecinchoxinic acid, $O<\begin{matrix}CHMe\cdot N{:}C_9H_6\cdot COOH\\ CHMe\cdot N{:}C_9H_6\cdot COOH\end{matrix}$, obtained by boiling a solution of ethylidenecinchonic acid in dilute alcohol for a long time in presence of air, crystallises from hot alcohol in colourless needles, melts at 206°, and is readily soluble in warm alcohol, but only very sparingly in chloroform, and almost insoluble in water and ether; it sublimes unchanged in long, colourless needles. The *sodium* salt, $C_{24}H_{20}N_2O_5Na_2 + Aq$, is readily soluble in alcohol and water, from which it separates in well-defined, efflorescent crystals. The *potassium* salt forms short, transparent prisms, and dissolves freely in

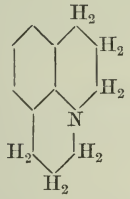
alcohol and water. The *silver* salt, $C_{24}H_{20}N_2O_5Ag_2$, is a moderately stable, crystalline powder.

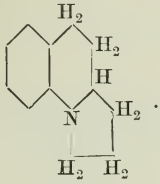
Cinchonic acid propobromide, $C_{10}H_7NO_2,PrBr$, crystallises from alcoholic ether in lustrous, colourless needles, melts at 218° with decomposition, and is readily soluble in alcohol and water. The corresponding additive products with isobutyl bromide and amyl iodide could not be obtained. F. S. K.

Action of Trimethylene Chlorobromide on Aromatic Amines and Amides. By G. Pinkus (*Ber.*, **25**, 2798—2806).—Gabriel and his pupils have shown that trimethylene chlorobromide acts on thioamides with formation of penthiazolines having the general formula $RC\lessdot^{S\cdot CH_2}_{N\cdot CH_2}\!>CH_2$. In the present paper, the author describes the results obtained by substituting amides for the thio-derivatives.

Formanilide and trimethylene chlorobromide react with one another at the boiling point of the latter, forming a mixture of two bases having the formulæ $C_{13}H_{12}N_2$ and $C_{12}H_{15}N$ respectively, carbonic oxide being also evolved. The former base is identical with the methenyldiphenylamidine described by Wallach, its formation being brought about by the action on the excess of formanilide of the hydrogen chloride set free during the process. The second base may be obtained much more readily and unmixed with the amidine by substituting aniline for formanilide.

The base contains a tertiary nitrogen atom, and hence both hydrogen atoms of the amido-group have been replaced, one halogen atom of each molecule of the chlorobromide having been eliminated with each of these hydrogen atoms; the remaining halogen atoms would most probably combine with hydrogen atoms in the benzene nucleus forming a compound having one of the following constitutional formulæ :—





That the base is in reality a derivative of tetrahydroquinoline is proved by the fact that it may also be obtained by the action of trimethylene chlorobromide on that compound; in order to ascertain which of the above formulæ is correct, the action of the chlorobromide on formorthotoluidide and formoparatoluidide was examined, the result showing that whilst the para-derivative readily yields an analogous base, the ortho-derivative behaves in a different manner. Hence the first of the above formulæ must be correct, for, as will be seen, no such compound can be formed if the ortho-position is already occupied, as it is in formorthotoluidide.

The base $C_{12}H_{15}N$ is also formed in small quantity by the re-

duction of Reissert's α-keto-γ-juloline (this vol., p. 883); this fully agrees with the above constitution, and the name of the substance, therefore, becomes, in accordance with Reissert's system, *julolidine*.

Julolidine is a colourless, crystalline mass which melts at 40°, boils with considerable decomposition at 280°, and becomes brownish-red after a time; the *hydrochloride*, $C_{12}H_{15}N,HCl$, crystallises in white prisms, is partially dissociated by water, and melts at 218°; the *hydriodide* melts at 219—222°, the *picrate* at 165°, and the *platinochloride* at 220°. The base gives a deep blood-red coloration with all oxidising agents; purple-red needles having a metallic lustre, sometimes separate out, but gradually become colourless. Towards methyl iodide, julolidine behaves as a tertiary base yielding a *methiodide* which forms colourless crystals, melts at 186°, and is not attacked by potash.

The base obtained from formoparatoluidide is an oil, but yields a crystalline *hydriodide*, $C_{12}NH_{14}Me,HI$, and shows reactions similar to those of julolidine. Formorthotoluidide, on the other hand, yields, with trimethylene chlorobromide, a salt having the formula $C_6H_4Me{\cdot}N(C_3H_6X)_2,HX$, X being partly chlorine and partly bromine. This substance only loses the remainder of the halogens with great difficulty, and then forms tetrahydrorthotoluquinoline, $C_{10}H_{13}N$ (compare Ziegler, Abstr., 1888, 609). The free base melts at 252°, the *hydrochloride* at 210°, the *picrate* at 168°, the *platinochloride* at 212°, and the *nitroso*-derivative at 136°.

Paramethoxyquinoline is also attacked by trimethylene chlorobromide with formation of *paramethoxyjulolidine*, $C_{12}NH_{14}{\cdot}OMe$, which is a pungent-smelling liquid; its *hydrochloride* separates from water in long needles, and from alcohol in compact crystals, melts at 188° with decomposition, and gives no coloration with ferric chloride; the *platinochloride* melts at 209—210°.

The action of trimethylene chlorobromide on benzenesulphanilide and of ethylene bromide on benzylamine was also examined, but in the first case no reaction takes place, and very little in the second.

H. G. C.

Cincholine and Fluoroline. By O. Hesse (*Annalen*, **271**, 95—100; compare Abstr., 1882, 1114; and Weller, Abstr., 1887, 979).—Cincholine, $C_{10}H_{21}N$, obtained from paraffin oil, and purified by means of its oxalate, is a highly refractive oil, with an odour recalling that of pyridine, and specifically lighter than water; it boils at 236—238°, and dissolves freely in ether, chloroform, and alcohol, but is almost insoluble in water. The oxalate, $(C_{10}H_{21}N)_2,C_2H_2O_4$, crystallises in colourless plates, and is only sparingly soluble in cold alcohol, and almost insoluble in cold water; the other salts do not crystallise.

Fluoroline, $C_{12}H_{13}N$, the volatile base previously described as hygrine, and supposed to have been obtained from (?) Trujillo coca (*Pharm. Zeit.*, 1887, 668) is probably derived from the coal-tar oil employed in extracting the alkaloïds, in spite of the fact that Giesel has also stated that the base can be obtained from Trujillo coca and from Java coca (*Pharm. Zeit.*, **36**, 420). It is a yellow oil, with a peculiar odour, like that of quinoline, and dissolves freely in ether,

alcohol, and chloroform, but only sparingly in cold water; it has a strongly alkaline reaction, and is readily soluble in dilute acids, the solutions showing a blue fluorescence. The *oxalate* crystallises in colourless needles, and is readily soluble in water and alcohol. The *hydrochloride* is crystalline and readily soluble in water. The *platinochloride*, $(C_{12}H_{13}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in small, pale yellow needles, loses its water at 100°, and is only sparingly soluble in cold water. F. S. K.

Glyoxaline. By F. Rung and M. Behrend (*Annalen*, **271**, 28—40). —The following experiments were undertaken with the object of throwing some light on the constitution of glyoxaline, but they were brought to a conclusion by the publication of Bamberger's papers (this vol., p. 632) on benzimidazoles.

Diazobenzeneglyoxaline, $C_3H_3N_2{\cdot}N_2Ph$, prepared by treating glyoxaline with diazobenzene chloride in ice-cold, aqueous solution, crystallises from dilute alcohol in red needles, melts at 177—178°, and is readily soluble in alcohol, ether, and chloroform, but only sparingly in water, and almost insoluble in light petroleum; it resinifies on exposure to the air, and is decomposed by boiling acids.

A compound of the composition $C_3H_3N_3O_2$, probably a *nitroglyoxaline*, is produced when glyoxaline is heated with a mixture of nitric acid and concentrated sulphuric acid; it separates from boiling alcohol in colourless needles, and is sparingly soluble in hot water and alcohol, insoluble in ether and chloroform, but soluble in glacial acetic acid and hydrochloric acid; it dissolves in alkalis yielding yellow solutions, from which it is precipitated unchanged on the addition of an acid; it forms a sparingly soluble silver derivative.

A crystalline additive product is formed when methylglyoxaline is warmed with ethyl chloracetate; it melts at 196—197°, and is very readily soluble in water; on adding platinic chloride to an aqueous solution of this substance, a crystalline salt of the composition $(C_8H_{13}N_2O_2Cl)_2,PtCl_4$ is obtained.

Glyoxaline also combines with ethyl chloracetate, yielding a syrupy product which is very readily soluble in water; in its aqueous solution platinic chloride produces a crystalline precipitate of the composition $C_{22}H_{34}N_4O_8,PtCl_6$. When the original syrupy product is digested with silver oxide in aqueous solution, it is converted into a crystalline substance of the composition $C_7H_8N_2O_4$, which decomposes when heated above 230—235°, but without melting; as the same compound can be obtained by heating glyoxaline with chloracetic acid at 100°, and then treating the product with silver oxide in aqueous solution, its constitution is probably expressed by the formula

$$COOH{\cdot}CH_2{\cdot}C_3H_3N_2{<}\begin{matrix}CH_2\text{–}\\O{\cdot}CO\end{matrix}{>}.$$

When the methiodide or ethiodide of methylglyoxaline is boiled with concentrated potash, it is decomposed with liberation of methylamine, no ammonia being formed. Methylglyoxaline propochloride is decomposed by boiling potash, yielding methylamine and formic acid in molecular proportion; methylglyoxaline amylochloride also

gives methylamine, whilst benzylglyoxaline methiodide yields benzylamine. F. S. K.

Cinnoline Derivatives. By M. Busch and M. Klett (*Ber.*, **25**, 2847—2853; compare v. Richter, Abstr., 1883, 1105).—Hydroxycinnoline (*loc. cit.*) is thus prepared:—The calculated quantity of sodium nitrite solution is added to orthamidophenylpropiolic acid, suspended in a mixture of equal volumes of concentrated hydrochloric acid and water (10 parts), and the hydroxycinnolinecarboxylic acid thus obtained is converted into hydroxycinnoline. O. Fischer's harmine (Abstr., 1889, 730) is, perhaps, dihydrocinnoline, but cinnoline itself is unknown, and the authors' attempts to prepare it by the action of numerous reducing agents on both hydroxycinnoline and on the chloro-derivative have proved unsuccessful.

Chlorocinnoline, $C_6H_4<\begin{matrix}CCl{:}CH\\ |\\ N{=}N\end{matrix}$, is obtained by slowly adding hydroxycinnoline to phosphoric chloride (4 parts) mixed with some phosphorus oxychloride, subsequently heating the mixture on the water-bath for an hour, and pouring it on to ice, whereby an aqueous solution is obtained. After adding alkali to the latter, it is extracted with ether, the colouring matters being removed from the ethereal solution by treating it with animal charcoal. The compound crystallises from light petroleum in long, white needles, melts at 79°, and is very readily soluble in alcohol. The chlorine is displaced by hydroxyl even on boiling the compound with water, and when silver nitrate is added to its aqueous solution the theoretical amount of silver chloride is precipitated. The hydrochloride forms white needles, and melts at 151°. *Anilidocinnoline*, $C_6H_4<\begin{matrix}C{\cdot}NHPh\\ |\\ N{=}N\end{matrix}>CH$, formed by gently warming the chloro-derivative with aniline, crystallises in brownish, lustrous needles, melts at 232°, and is sparingly soluble in ether. *Paratoluidocinnoline* melts at 215°.

Ethoxycinnoline, $C_6H_4<\begin{matrix}C(OEt){:}CH\\ |\\ N{=}N\end{matrix}$, is obtained by gently warming hydroxycinnoline with sodium ethoxide in alcoholic solution; protracted heating causes decomposition. The compound crystallises from light petroleum in small, colourless, felted needles, melts at 106°, and is very readily soluble in water. A. R. L.

β-Succinylphenylhydrazide or 1-Phenyl-3 : 6-orthopiperazone. By A. Michaelis and R. Hermens (*Ber.*, **25**, 2747—2752).—*β-Succinylphenylhydrazide* or 1-*phenyl*-3 : 6-*orthopiperazone*,

$$\begin{matrix}CH_2{\cdot}CO{\cdot}NPh\\ |\\ CH_2{\cdot}CO{\cdot}NH\end{matrix},$$

is obtained by the action of succinic chloride on sodium phenylhydrazide. This substance (isomeric with Hotte's α-succinylphenylhydrazide) crystallises from hot water in transparent crystals melting at 199°. It reduces Fehling's solution when heated, and does not give the Bülow colour reaction with sulphuric acid and potassium chromate. It is sparingly soluble in cold water or boiling alcohol, readily

in boiling water or glacial acetic acid. It is soluble in aqueous alkalis and in ammonia, and does not form a nitroso-derivative, thus resembling Hotte's corresponding β-phthalylphenylhydrazide. When heated with excess of acetic anhydride, it yields the *monacetyl* derivative; this crystallises in colourless scales, which darken at 172°, and melt at 179°. It is very sparingly soluble in boiling water, more soluble in boiling alcohol. Cold dilute alkali does not dissolve it, but when hot causes its decomposition.

Attempts to produce the above piperazone by the hydrolysis of ethyl succinate phenylhydrazide proved unavailing, the α-hydrazide, $\begin{matrix}CH\cdot CO\\ |\\ CH\cdot CO\end{matrix}>N\cdot NHPh$, being formed.

Ethyl succinic chloride, $COOEt\cdot CH_2\cdot CH_2\cdot COCl$, was obtained by the action of phosphoric oxychloride on sodium ethyl succinate,

$$COOEt\cdot C_2H_4\cdot COONa.$$

It is a colourless, mobile, highly refractive liquid, boiling at 144° under 90 mm. pressure. It has a pungent smell, fumes in the air, and is only slowly decomposed by cold water. When distilled under atmospheric pressure, it is decomposed into ethyl chloride and succinic anhydride. When this chloride (1 mol.) is treated with phenylhydrazide (2 mols.), *ethyl succinate phenylhydrazide*,

$$COOEt\cdot C_2H_4\cdot CO\cdot NH\cdot NHPh,$$

is formed. This substance crystallises from hot water in white needles, soluble in alcohol, but only sparingly so in ether. It melts at 107°, reduces Fehling's solution, and shows the Bülow reaction. When it is dissolved in hot dilute potash and the solution, on cooling, acidified with hydrochloric acid, a substance of the formula $C_{20}H_{22}N_4O_3$ is formed, which crystallises in colourless needles melting at 137°, and reduces Fehling's solution. When heated to 170°, this compound yields Hotte's α-succinyl phenylhydrazide; and is, therefore, probably the anhydride, $O(CO\cdot C_2H_4\cdot CO\cdot NH\cdot NHPh)_2$. The authors find that when pure, Hotte's α-hydrazide crystallises at 158° (Hotte 155°).

L. T. T.

New Synthesis of Ketoquinazolines and Thioquinazolines. By M. Busch (*Ber.*, **25**, 2853—2860).—*Phenyltetrahydroketoquinazoline*, $C_6H_4<\begin{matrix}NH\cdot CO\\ |\\ CH_2\cdot NPh\end{matrix}$, separates, together with orthamidobenzylaniline hydrochloride, when a 20 per cent. solution of carbonyl chloride (0·5 mol.) in toluene is added to an ethereal solution of orthamidobenzylaniline; the mixture is then shaken with water, the solvent distilled off, and the compound crystallised from dilute alcohol. It crystallises from ethyl acetate in colourless, translucent, four-sided tables, melts at 189°, and is indifferent both towards acids and towards alkalis.

Phenyltetrahydrothioquinazoline, $C_6H_4<\begin{matrix}NH\cdot CS\\ |\\ CH_2\cdot NPh\end{matrix}$, is prepared by boiling orthamidobenzylaniline with carbon bisulphide (3 parts) and an equal volume of alcoholic potash, in a reflux apparatus, for an hour. After distilling off the liquid and crystallising the residue

from alcohol, the compound is obtained in colourless needles or large, translucent plates almost insoluble in ether; its melting point (about 245°) is not sharp. If heated with alcohol and mercuric oxide in a sealed tube at 150° for five hours, it gives the above-described keto-compound; whilst, on reduction with sodium ethoxide, phenyltetrahydroquinazoline (Abstr., 1890, 73), which is now found to melt at 119°, is produced.

Paratolyltetrahydroketoquinazoline, $C_6H_4<\begin{matrix}NH\cdot CO\\ CH_2\cdot N\cdot C_6H_4Me\end{matrix}$, melts at 218—220°, and *paratolyltetrahydrothioquinazoline*,

$$C_6H_4<\begin{matrix}NH\cdot CS\\ CH_2\cdot N\cdot C_6H_4Me\end{matrix},$$

at 235°. The latter yields the keto-compound on oxidation with mercuric oxide, whilst reduction with sodium ethoxide converts it into paratolyltetrahydroquinazoline (*loc. cit.*).

Tetrahydrothioquinazoline, $C_6H_4<\begin{matrix}NH\cdot CS\\ CH_2\cdot NH\end{matrix}$, is obtained from orthamidobenzylamine and carbon bisulphide; it crystallises from alcohol in nodular aggregates of leaflets, and melts at 210—212°.

A. R. L.

Action of Formaldehyde on Orthodiamines. By O. Fischer and H. Wreszinski (*Ber.*, **25**, 2711—2715).—The tertiary anhydrobases (imidazoles), of which methylmethenylphenyleneamidine, melting at 33° (Abstr., 1889, 731), is the simplest member, are formed when an excess of formaldehyde is added to a faintly acid solution of an orthodiamine hydrochloride, the mixture being, after a while, rendered alkaline, and the base extracted with ether. If, however, the formaldehyde is added to a neutral solution of the orthodiamine, bases polymeric with the last-mentioned are obtained.

The *base*, $C_{16}H_{16}N_4$, is prepared by adding 50 per cent. formaldehyde (3 grams) to a hot solution of orthophenylenediamine (2 grams) in alcohol (15 grams), and boiling the mixture for a minute; it separates on adding water, and when crystallised from ether forms colourless, thick tables, melts at 144°, and is almost insoluble in water; it probably has the constitution $\begin{matrix}C_6H_4\cdot N{-}CH\cdot NMe\\ NMe\cdot CH\cdot N{-}C_6H_4\end{matrix}$. The *platinochloride* forms yellow, lustrous needles, and melts at 240°. In a similar manner there are obtained from diamidotoluene [Me : $(NH_2)_2$ = 1 : 3 : 4], a base, $C_{18}H_{20}N_4$, melting at 222°, and from $\alpha\beta$-diamidonaphthalene a base, $C_{24}H_{20}N_4$, melting at 165°.

Methenylnaphthaleneamidine, $C_{10}H_6<\begin{matrix}NH\\ {-}N\end{matrix}>CH$, is produced by boiling $\alpha\beta$-diamidonaphthalene with formic acid; it crystallises from ether in large plates, melts at 174°, and is sparingly soluble in water. A *methyl* derivative is obtained when the last-described base is heated under pressure with methyl iodide (1 mol.) and wood spirit (10 parts) for 5—6 hours; it is a bright, yellow oil, which boils at 286°, and its solution in alcohol exhibits a beautiful blue fluorescence.

A. R. L.

Nicotine. By A. Pinner (*Ber.*, **25**, 2807—2821).—By the action of bromine on free nicotine, large quantities of resinous products are formed; whilst the action of bromine on a solution of nicotine in acetic acid or hydrobromic acid gives rise in the first place to an oily additive product from which the bromine is eliminated by treatment with sulphurous acid. In acetic acid solution the reaction quickly goes further; hydrogen bromide is formed, and the product contains the two compounds $C_{10}H_8N_2Br_2$ and $C_{10}H_8N_2Br_2O_2$, of which the former yields the well crystallised perbromide, $C_{10}H_8N_2Br_2,HBr_3$, described by Huber (*Annalen*, **131**, 257), and Cahours and Etard (*Compt. rend.*, **90**, 1315; *Bull. Soc. Chim.*, **34**, 457); the latter yields a colourless hydrobromide, $C_{10}H_8N_2Br_2O_3,HBr$, formerly obtained in an impure condition by Laiblin.

The perbromide, $C_{10}H_8N_2Br_2,HBr_3$, is obtained by adding bromine ($3\frac{1}{2}$—4 parts), dissolved in acetic acid (4—5 parts), to a solution of nicotine in acetic acid (5—6 parts). The oily product first formed dissolves on allowing the mixture to remain, or on gently warming it at 50—60°. The perbromide crystallises from the clear solution after two days in monosymmetric, chrome-red scales or flat, yellowish-red needles, is easily soluble in warm acetic acid, sparingly so in water, melts at 163° with decomposition, smells of bromine, which it loses on drying, and is decomposed by boiling with water with evolution of bromine and production of a colourless solution, which probably contains the base as hydrobromide. The complete combustion of the substance is extremely difficult, and as the numbers obtained on analysis do not agree very well with those demanded by theory, the above composition was also proved by titrating the product with sulphurous acid, by estimating the amount of hydrogen bromide formed in the reaction with soda solution, and also by precipitation with silver nitrate. The results obtained in this way agree with those required by the formula given.

The free base, dibromodehydronicotine, $C_{10}H_8N_2Br_2$, is obtained by treating the perbromide with ammonia. The *hydrobromide* is very easily soluble in water. The *picrate*, $C_{10}H_8N_2Br_2,C_6H_2(NO_2)_3{\cdot}OH$, is obtained by heating the perbromide with water, and adding picric acid to the aqueous solution; also by adding bromine (6—8 atoms) to a solution of nicotine in hydrobromic acid, boiling until the mixture is free from bromine, and then adding picric acid, or by reducing the perbromide with sulphurous acid and adding picric acid. It crystallises from water in large, lustrous, highly refractive, yellow prisms, darkens at 177°, melts at 180°, and then decomposes with much frothing. The *platinochloride* crystallises in long, yellow needles, darkens at 200°, does not melt at 250°, and is very sparingly soluble in water.

Dibromodioxydehydronicotine hydrobromide, $C_{10}H_8N_2O_2Br_2,HBr$, is obtained by heating nicotine (10 grams) with aqueous hydrobromic acid (20 per cent., 25 grams) and bromine (25 grams) in a sealed tube for 10—12 hours on the water-bath. It crystallises from water in slender, white needles, or colourless, lustrous, flat prisms, begins to darken at 200°, decomposes on further heating, and is easily soluble in hot water, sparingly so in the cold. The *free base* is obtained by adding alkali to a solution of the salt. It is obtained in small, nodular

crystals, melts at 196° with decomposition, and is soluble in acids, alkalis, and the alkaline earths. When the free base is oxidised with alkaline permanganate, it yields nicotinic acid.

Dibromodehydronicotine, when treated with strong bases, yields methylamine, oxalic acid, and a compound containing nitrogen; the latter has not yet been isolated. The crystallised perbromide is treated with a slight excess of sulphurous acid, and to the colourless liquid thus obtained an excess of barium hydroxide is added, the mixture filtered, and then heated to boiling, and distilled with steam as long as the distillate is alkaline. Methylamine hydrochloride is easily obtained from the filtrate in the theoretical quantity, supposing that one nitrogen atom is eliminated in the form of methylamine, and barium oxalate is found in the residue.

The author is engaged in attempting to isolate the third decomposition product of dibromodehydronicotine. E. C. R.

Alkaloïds of Belladonna. By O. Hesse (*Annalen*, **271**, 100—126).—The greater part of this paper consists of a description of well-known salts of hyoscyamine, atropine, and hyoscine, and of a discussion of the results of other chemists' work on the alkaloïds of belladonna.

Hyoscine has the composition $C_{17}H_{21}NO_4$, and not $C_{17}H_{23}NO_3$, as supposed by Ladenburg and Merck; it melts at about 55°, and dissolves freely in ether, chloroform, and alcohol, but is only moderately easily soluble in water; its specific rotatory power in alcoholic solution at 15° is $[\alpha]_D = -13{\cdot}7°$.

The author proposes that Ladenburg's pseudotropine or hydroxytropine should be called *oscine;* the composition of oscine is $C_8H_{13}NO_2$, not $C_8H_{15}NO$. *Benzoyloscine*, $C_{15}H_{17}NO_4$, prepared by heating oscine at 80—100° with an equal weight of water and a large excess of benzoic anhydride, crystallises from chloroform in needles, melts at 59°, and is readily soluble in ether, alcohol, chloroform, and acids, and moderately easily in water. The *aurochloride*, $C_{15}H_{17}NO_4,HAuCl_4$, crystallises in small, yellow needles, and melts at 184°.

Atropamine platinochloride (compare Abstr., 1891, 228) crystallises in yellow scales, and melts at 203—204° with decomposition.

F. S. K.

Hyoscine (Scopolamine). By E. Schmidt (*Ber.*, **25**, 2601—2607).—A reply to Ladenburg (this vol., p. 1366).

Berberis Alkaloïds. Berberine and Hydroberberine. By E. Schmidt (*Arch. Pharm.*, **230**, 287—291).—The author has caused fresh experiments to be made which confirm and amplify those previously carried out by H. Schreiber (*Inaug. Diss.*, Marburg, 1888), and R. Gage (Abstr., 1890, 1012; and 1891, 332). These experiments were carried out by C. Link, and are described in the following abstract.

C. F. B.

Berberine and Hydroberberine. By C. Link (*Arch. Pharm.*, **230**, 291—320).—When an aqueous solution of berberine sulphate is treated with excess of bromine in the cold, berberine tetrabromide hydrobromide, $C_{20}H_{17}NO_4,Br_4,HBr$, is formed; but this, when heated at 100° or treated with cold alcohol, loses 2 atoms of bromine and

forms the dibromide hydrobromide, which, when boiled with alcohol, loses 2 atoms more, yielding berberine hydrobromide, $C_{20}H_{17}NO_4,HBr + 2H_2O$.

Hydroberberine tetrabromide hydrobromide, $C_{20}H_{21}NO_4,Br_4,HBr$, is formed when hydroberberine, either in sulphuric acid or in chloroform solution, is treated with bromine. When heated at 100°, or when boiled with alcohol, it is converted into the dibromide, $C_{20}H_{21}NO_4Br_2$, which in the latter case crystallises with $3H_2O$. The dibromide, when heated with alcoholic potash, loses CH_3Br, one of the two methoxyl groups being destroyed, and yields a compound $C_{19}H_{18}NO_4Br$, which is not a hydrobromide, for it does not give silver bromide with silver nitrate, but a crystalline compound $C_{19}H_{18}NO_4Br,AgNO_3$. Hydroberberine dibromide still has basic properties, for it forms a platinochloride, $(C_{20}H_{21}NO_4Br)_2,H_2PtCl_6$. When reduced with zinc and hydrochloric acid, it yields hydroberberine.

Various compounds of hydroberberine with ethyl iodide and bromide, and of these with gold and platinum chlorides, were prepared; these are tabulated below. Hydroberberine ethiodide, when treated with silver oxide, yielded an ethylammonium base, $C_{20}H_{21}NO_4Et{\cdot}OH + 4H_2O$, melting at 163—165°. When this is heated in a current of dry hydrogen, it loses not 4 but 5 mols. H_2O, ethylhydroberberine, $C_{20}H_{20}EtNO_4$, being presumably formed. This substance crystallises with $3H_2O$, when it melts at 240—245°; when dried at 100°, it loses $2H_2O$, leaving $C_{20}H_{20}EtNO_4 + H_2O$, or $C_{20}H_{20}NO_4,EtOH$. It also crystallises from a solution in chloroform and alcohol with $4H_2O$, and then loses $3H_2O$ when dried at 100, leaving the same compound as before. This substance is quite distinct from the ethyl base of hydroberberine from which it was prepared; it is not, as was to be expected, a tertiary base, but is a quaternary compound, and gives no alkaline reaction. With ethyl iodide, for example, it forms not an ethyl iodide additive compound, but a hydriodide from which a base cannot be set free by the action of potash. A number of halogen acid derivatives of ethylhydroberberine (tabulated below) were prepared for comparison with the corresponding ethyl halogen derivatives of hydroberberine.

Hydroberberine ethohydroxide, $C_{20}H_{21}NO_4,EtOH + 4H_2O$, m. p. 163—165°.

Hydroberberine ethochloride, $C_{20}H_{21}NO_4,EtCl + 2\frac{1}{2}H_2O$, m. p. 225—226°.

Hydroberberine ethaurochloride, $C_{20}H_{21}NO_4,EtAuCl_4$, m. p. 180—181°.

Hydroberberine ethoplatinochloride, $(C_{20}H_{21}NO_4)_2,Et_2PtCl_6$, m. p. 229—230°

Hydriodide of ethyl base, $C_{20}H_{21}NO_4,EtI + H_2O$, m. p. 227—228°.

Ethylhydroberberine, $C_{20}H_{20}EtNO_4 + 4H_2O$, m. p. 240—245°.

Ethylhydroberberine chloride, $C_{20}H_{20}EtNO_4,HCl + 2\frac{1}{2}H_2O$, m. p. 261—263°.

Ethylhydroberberine aurochloride, $C_{20}H_{20}EtNO_4,HAuCl_4$, m. p. 184—185°.

Ethylhydroberberine platinochloride, $(C_{20}H_{20}EtNO_4)_2,H_2PtCl_6$, m. p. 220—221°.

Hydriodide of ethylhydroberberine, $C_{20}H_{20}EtNO_4,HI$, m. p. 241—242°.

Hydrobromide of ethyl base, $C_{20}H_{21}NO_4,EtBr$, m. p. 250—251°.

Hydrobromide of ethylhydroberberine, $C_{20}H_{20}EtNO_4,HBr$, m. p. 245—246°.

Hydroberberine ethonitrate, $C_{20}H_{21}NO_4,EtNO_3 + H_2O$, m. p. 243—244°.

Ethylhydroberberine nitrate, $C_{20}H_{20}EtNO_4,HNO_3 + 2H_2O$, m. p. 131—132°.

It was further observed that, although an alcoholic solution of iodine oxidises hydroberberine to berberine hydriodide, it converts the hydroberberine ethylammonium base into hydroberberine ethiodide, and ethylhydroberberine into its hydriodide. C. F. B.

Lysine. By E. Drechsel and T. R. Krüger (*Ber.*, **25**, 2454—2457).—The platinochloride, $C_6H_{14}N_2O_2,H_2PtCl_6 + C_2H_6O$, obtained from caseïn, was dissolved in water, freed from alcohol by distillation, and from platinum by means of hydrogen sulphide, and the acid solution of the dihydrochloride thus obtained was heated on the water-bath with the calculated quantity of sulphuric acid until all the hydrochloric acid had been driven off. The residual syrup, which crystallised on cooling, was dissolved in hot water, the sulphuric acid accurately precipitated with barium hydroxide, and the solution filtered and evaporated to crystallisation. Not lysine, but lysine carbonate, or perhaps more properly, lysine lysinecarbamate, $2C_6H_{14}N_2O_2 + CO_2$, was obtained; this substance loses its carbonic anhydride when heated at 110° in a current of air freed from that gas.

If the dihydrochloride is evaporated to dryness on the water-bath with excess of milk of lime, and the residue distilled in a current of hydrogen, various basic products are obtained. In some experiments the aqueous portion of the distillate was treated with soda and benzoic chloride, and an oil obtained which crystallised on cooling to a substance which melts at 42·6°, and when boiled with water or alkalis or heated in hydrogen to 120°, yields benzoic acid and a substance apparently of a basic nature. C. F. B.

Constitution of Peptones. By P. Schützenberger (*Compt. rend.*, **115**, 208—213).—Blood fibrin from the horse was converted into peptone by the action of extractive pepsin in presence of hydrochloric acid. The solution has all the properties of proteïd peptone, and when evaporated in a dry vacuum it yields a yellowish friable mass of *fibrin-peptone*. When its solution is mixed with excess of ammonium sulphate, it yields a viscous precipitate as observed by Kühne.

During conversion into peptone, the fibrin combines with 3·97 per cent. of water; after drying in a vacuum, its composition, exclusive of the ash, is C, 49·18; H, 7·09; N, 16·33; O and S, 27·40. These numbers agree closely with those obtained by Kühne and Chittenden with carefully purified ampho-peptone from blood fibrin. The formation of fibrin-peptone may be represented by the equation $C_{56}H_{92}N_{16}O_{20} + 3H_2O = C_{56}H_{98}N_{16}O_{23}$.

When fibrin-peptone is heated for six hours at 150—180° with three times its weight of barium hydroxide, it yields ammoniacal nitrogen 4·1, carbonic anhydride 5·94, acetic acid 3·16, and solid re-

sidue 87·82 per cent., the sum of the products being practically identical in weight with the original peptone, a fact which seems to indicate that no combination with water takes place. The solid residue, exclusive of the ash, has the composition C, 47·52; H, 7·61; N, 12·93; O, 31·94; and the loss of carbon and nitrogen seems to be due to the formation of volatile bases of the pyrroline or pyridine groups, as observed in the case of other proteïds. The decomposition of the peptone may be represented by the equation $C_{56}H_{98}N_{16}O_{32} + 6H_2O = 2CO_2 + 4NH_3 + \frac{1}{2}C_2H_4O_2 + C_6H_7N + C_{47}H_{89}N_{11}O_{34}$. The ureides present in the fibrin remain in the fibrin peptone, and the decomposition of the latter in presence of baryta is similar to that of fibrin itself and other proteïds. C. H. B.

Molecular Weight of the Peptones. By G. Ciamician and C. U. Zanetti (*Gazzetta*, **22**, 449—452; compare Paal, this vol., p. 896).—The authors prepared pure peptone by dissolving the commercial substance in water, adding potassium ferrocyanide and acetic acid, and fractionally precipitating the solution with alcohol. The separated peptone was repeatedly (10 times) dissolved in water and precipitated by alcohol; it was finally dried over sulphuric acid.

Experiments made by the cryoscopic method in aqueous solutions on two samples of commercial peptone, after treating as above, gave the molecular weights as 529—555 and 317—344 respectively.

W. J. P.

Nucleïn. By H. Malfatti (*Zeit. physiol. Chem.*, **17**, 8—9; compare this vol., p. 224).—In a former paper the statement was made that nucleïc acid prepared from Liebermann's nucleïn can unite with guanine, forming a compound like the nucleïc acids obtained from natural nucleïn. Several repetitions of the experiments led, however, to negative results. W. D. H.

Pupin. By A. B. Griffiths (*Compt. rend.*, **115**, 320—321).—*Pupin*, $C_{14}H_{20}N_2O_5$, is a colourless, amorphous substance, obtained from the skin of the pupæ of various lepidoptera (*Pieris brassicæ*, *napi*, and *rapæ*, Latreille, and *Plusia gamma*, *Mamestra brassicæ*, and *Noctua pronuba*, Linn.), where it is secreted after the last change. The skins are boiled with aqueous soda, washed in succession with dilute acid, water, alcohol, and ether, and finally dissolved in strong hydrochloric acid. The crude product is precipitated by water and purified by repeated precipitation from acid solution.

Pupin dissolves in mineral acids, but not in neutral solvents. When boiled with strong mineral acids for a long time, it is hydrolysed to leucine and carbonic anhydride, each molecule yielding two of each of these substances. Jn. W.

Physiological Chemistry.

Air Vitiated by Respiration. By J. Haldane and J. L. Smith (*J. Pathol. and Bacteriol.*, **1**, 168—186).—From experiments on human beings the following conclusions are drawn:—

1. The immediate danger from breathing air highly vitiated by respiration arises entirely from the excess of carbonic anhydride and deficiency of oxygen, and not from any special poison. Experiments on animals, consisting of injecting the products of respiration into them (obtained by condensing the products of respiration expired into a Liebig's condenser), caused no more ill-effect than distilled water.

2. Excess of carbonic acid rather than deficiency of oxygen is the more potent cause of hyperpnœa and headache.

A practical conclusion drawn from these experiments is, that the unpleasantness of close rooms is due rather to the effect produced through the sense of smell; and, therefore, that personal cleanliness is more important than ventilation; in fact, the odours that arise may be removed by other means than the excessive ventilation now considered so necessary. W. D. H.

Formation of Sugar from Peptones in Blood. By R. Lépine (*Compt. rend.*, **115**, 304—305).—Purified commercial peptone (0·2 to 0·5 gram) is dissolved in the recent arterial blood (40 grams) of a healthy dog, defibrinated, or better, treated with sodium fluoride. In less than an hour the peptone is no longer to be recognised by the colorimetric reaction with copper sulphate, and the amount of sugar in the blood is found to have increased. With the temperature at 39°, or better, at 55—60°, peptone seems to yield nearly one-tenth of its weight of sugar. Jn. W.

Iron in the Fœtal Organism. By G. Bunge (*Zeit. physiol. Chem.*, **17**, 63—66).—In two former communications (Abstr., 1889, 789; this vol., p. 516) it has been shown that certain organs of the new-born mammal contain a store of iron, which is gradually used up in the formation of the iron-containing principles of the body, the milk containing insufficient iron for the purpose. In young guinea pigs this is not so marked, as very soon after birth their milk diet is supplemented by vegetable food rich in iron. Young cats, dogs, and rabbits, live longer on milk only. The rabbit is born blind, and otherwise immature, the guinea pig is covered with warm fur, and its eyes are open. One must, therefore, for fair comparison, examine the guinea pig in a condition corresponding to that of the new-born rabbit; that is, the fœtal guinea pig must be removed from the uterus. It is then found that the theory is fully confirmed; the guinea pig, like the rabbit, has the highest relative amount of iron in its body at the time of birth; the amount of iron is directly related to that in its food. W. D. H.

Iron in the Liver. By G. Bunge (*Zeit. physiol. Chem.*, **17**, 78—82).—In order to estimate the iron in the liver it is, above all things, necessary to have it blood free. This can only be done during life; salt solution being passed through a cannula into the portal system in anæsthetised animals; the fluid is allowed to escape by the hepatic artery and vena cava inferior. The liver is removed and weighed, but only those portions which are perfectly pale, and give no red colour after soaking in distilled water, are taken for iron analyses. The amount of iron in milligrams per 100 grams of liver in 10 analyses (dogs and cats) were, 8·7, 1·0, 2·5, 2·6, 4·7, 4·7, 35·5, 5·2, 7·0, 6·4. The high number, 35·5, was in a very young animal, and contrasts forcibly with the rest, which were full grown. Investigations in the same direction with other organs are in progress.

W. D. H.

Horse Fat. By C. Amthor and J. Zink (*Zeit. anal. Chem.*, **31**, 381—383).—See this vol., p. 1533.

Myristic Acid in Ox Gall. By Lassar-Cohn (*Zeit. physiol. Chem.*, **17**, 67—77).—Myristic acid is obtained by fractional precipitation with barium acetate from the acids of ox bile. The percentage is 0·004. This acid has been hitherto found in eight plants, and in spermaceti. Whether it occurs in ordinary fat in small quantities is now under investigation. W. D. H.

Influence of Hot Baths on the Excretion of Nitrogen and Uric Acid from the Human System. By E. Formanek (*Monatsh.*, **13**, 467—481).—A single hot air or vapour bath does not cause any perceptible change in the excretion of nitrogen from the system, but if baths be taken on two consecutive days, the excretion of nitrogen is found to increase on the second day, the increase continuing until the day following. The same thing holds also for the excretion of uric acid. A temporary raising of the temperature of the body is, apparently, therefore, of little effect in this respect, it being necessary to maintain the action for some time before change is noticed.

H. C.

The Excretion of Nitrogen in Urine. By G. Gumlich (*Zeit. physiol. Chem.*, **17**, 10—14).—Analytical data of a large number of experiments with urine are given in tables or expressed in curves. The points investigated were, (1) the total nitrogen; (2) the nitrogen in ammonia; (3) the nitrogen left after precipitating by phosphotungstic acid; (4) the nitrogen of the so-called "extractives," that is, (1) − (2 + 3).

With different diets, there were found:—

1. A relatively large increase and diminution of urea with meat and vegetable food respectively.

2. A relative increase of ammonia with vegetable food. There was no change with animal food only.

3. A large relative diminution and increase of extractives with meat and vegetable diet respectively.

A large number of morbid urines were also examined. In febrile disorders there was a relative lessening of urea, an increase of ex-

tractives and of ammonia. In diabetes, all cases showed a relatively high percentage of ammonia; the amount of extractives and urea, as in healthy persons, varied with the diet.

In cases of liver cirrhosis, severe anæmia, and heart failure, there was relative lessening of urea, and increase of ammonia and extractives.

In cases of kidney disease, there was a lessening of total nitrogen, and an absolute and relative increase of ammonia. In uræmia, the urea excreted varies but little, but the extractives almost disappear: these substances appear to be retained in the tissues. The urea excreted in kidney disease is relatively great.

In healthy and sick persons, the excretion of extractives is increased if the body weight falls. It appears that the katabolism of tissue elements yields more extractives relatively than the decomposition of nitrogenous food stuffs. W. D. H.

Reducing Agents in Normal Human Urine. By G. S. Johnson (*Chem. News*, **66**, 91).—In correcting a misquotation in Neubauer and Vogel's *Analyse des Harns*, p. 57, the author points out that, when removing reducing substances from urine by means of mercuric chloride, he disposes of the excess of mercury by adding ammonia solution cautiously until precipitation is complete; under these circumstances both the solution, and the precipitate when decomposed by hydrogen sulphide under water, are free from substances reducing copper oxide. He recognises that when hydrogen sulphide is used to remove the excess of mercury, a decidedly reducing solution is produced. D. A. L.

Occurrence of Acetyl Derivatives in the Urine of Animals after Ingestion of Aldehydes. By R. Cohn (*Ber.*, **25**, 2457—2470).—Some time since (Jaffé and Cohn, Abstr., 1887, 1032) it was discovered that when dogs or rabbits are fed with furfuraldehyde, a Perkin's synthesis takes place, the furfuraldehyde condensing with acetic acid to form furfuracrylic acid, which leaves the body in combination with glycocine, occurring as furfuracryluric acid in the urine. Attempts to discover analogous syntheses have failed. Benzaldehyde is not converted into cinnamic acid; indeed, the latter substance, if introduced into the organism, leaves it as benzaldehyde. Thiophenaldehyde, administered to a dog, left the system as thiophenuric acid, partly as such, and partly in combination with carbamide. No thienylacrylic acid was found; and indeed this substance, when administered to a rabbit, was found to undergo decomposition, leaving the organism as thiophenuric acid. Further, in the cases of acetaldehyde, paraldehyde, chloral hydrate, and vanillin, no condensation with acetic acid was observed.

In some further experiments, however, with the nitrobenzaldehydes, it was found that acetic acid does play a part in the reaction, forming acetamido-derivatives.

When a dog is fed with metanitrobenzaldehyde, the latter is converted into metanitrohippuric acid, and leaves the organism partly as such, partly in combination with carbamide. If, however, rabbits

are experimented on, in addition to metanitrobenzoic and metanitrohippuric acids, metacetamidobenzoic acid is found in the urine. If metamidobenzoic acid is administered, no metacetamidobenzoic acid is formed, but uramidobenzoic acid.

Orthonitrobenzaldehyde, administered to rabbits, is for the greater part destroyed; a small quantity is converted into orthonitrobenzoic acid.

When paranitrobenzaldehyde is administered, a substance of the composition $C_{16}H_{14}N_2O_7$ makes its appearance in the urine. This substance forms colourless, spherical aggregates of small needles, fantastically disposed at the edges; it is rather insoluble in ether, soluble in boiling alcohol, and very slightly soluble in boiling water. It possibly has the constitution $COOH{\cdot}C_6H_4{\cdot}NO_2,NHAc{\cdot}C_6H_4{\cdot}COOH$, being a molecular compound of paranitrobenzoic and paracetamidobenzoic acids. When distilled, it gives off acetic acid; if heated at 150° in a sealed tube with hydrochloric acid, or when boiled with hydrochloric acid or barium hydroxide, it yields paranitrobenzoic acid; whilst reduction with ferrous hydroxide converts it into paracetamidobenzoic and paramidobenzoic acids. It can be synthesised by mixing hot solutions of paranitro- and paracetamido-benzoic acids, but is not formed by the loss of a molecule of water between these, for in that case the formula $C_{16}H_{14}N_2O_7$ would require the presence of 1 mol. of water of crystallisation, whereas it loses no water when heated at 150°, although it volatilises to some extent. In solution, it dissociates; the solution giving a lowering of the freezing point corresponding to a mixture of its two constituents. The solid substance is not, however, a mere mixture, but a true chemical compound, and that for the following reasons. It is formed when solutions of its two constituents are mixed, in proportions of either 1 : 2, 1 : 1, or 2 : 1; it cannot be separated into its constituents by fractional crystallisation, and when its silver salt is precipitated in three successive fractions, the third fraction contains the same percentage of silver as the first. It is a molecular compound of a novel and interesting type. Probably the two molecules are united by their nitrogen atoms. C. F. B.

Sulphates and Ethereal Hydrogen Sulphates in the Urine during Diarrhœa. By S. T. Bartoschewitsch (*Zeit. physiol. Chem.*, **17**, 35—57).—Full analytical details support the following conclusions:—The absolute and relative quantity of the preformed sulphates (a) and the ethereal hydrogen sulphates (b) are smaller during diarrhœa than normal, but the fractions $\frac{a+b}{b}$ or $\frac{a}{b}$ are smaller.

In calomel diarrhœa, the disinfection produced by the drug lessens b; this is not true for all purgatives, as castor oil increases b and lessens the fraction $\frac{a+b}{b}$. From this it appears that there are two classes of purgatives, those which disinfect the intestines and those which do not.

The diagnostic importance of such observations is not great, except that careful experimentation might sometimes lead to the detection of

those cases of malingering when diarrhœa has been artificially produced. W. D. H.

Hæmatoporphyrinuria. By A. E. Garrod (*J. Pathol. and Bacteriol.*, **1**, 187—197).—Small quantities of hæmatoporphyrin are present in healthy urine. Increase occurs in many diseases: some infective, others (as many cases of liver disease) not so. Anæmia does not constantly increase the amount, and in febrile diseases, the amount is not proportional to the severity of the attack.

W. D. H.

Physiological Action of Pentoses. By W Ebstein (*Virchow's Archiv*, **129**, 401—412).—In view of the dieting of diabetic patients, it is necessary to investigate the physiological action of various forms of sugar; and the present research relates to the two pentaglucoses or pentoses ($C_5H_{10}O_5$), xylose and arabinose.

These substances reduce Fehling's solution, Nylander's reagent, and form osazones with phenylhydrazine. They also give the following characteristic reactions:—(1.) By distillation with hydrochloric acid they yield furfuraldehyde. (2.) A solution mixed with an equal volume of concentrated hydrochloric acid and then with a solution of phloroglucinol in equal parts of hydrochloric acid and water, and warmed, gives a beautiful red colour, which gives a dark absorption band to the right of the D line. Most urines give a deep colour with these reagents, but the characteristic absorption band is not shown.

Xylose, dissolved in water or coffee, or in the solid state mixed with the food, was given to various people. The amount in the urine was estimated by Fehling's solution (1 milligram xylose = 1·9 milligrams copper), after any glucose that might have been present had been removed by fermentation with yeast. It appears that xylose is not assimilated, even when taken in very small quantity, and it can be recognised in the urine within an hour or two after the administration of 0·5 gram. This is true both for healthy and diabetic persons. One received 25 grams of xylose; in the next 24 hours 9·5 grams were found in the urine, and the excretion continued for the two following days.

Arabinose (1 milligram = 1·95 milligrams copper) gave practically the same results.

The use of fruit, such as pears, that contain pentosanes, the mother substances of pentoses, may give the characteristic tests for pentoses in the urine. It is, of course, important not to confound such a temporary condition with diabetes. W. D. H.

Pharmacological Investigations of Ketones and Acetoximes. By H. Paschkis and F. Obermayer (*Monatsh.*, **13**, 451—466).—In their physiological effects, the ketones of the fatty series resemble the alcohols, producing narcosis and decrease of blood pressure. In strength of action, the different ketones are by no means equal, this property being chiefly determined by the nature of the alkyl groups present in the molecule. In the case of the acetoximes, it was at first supposed that these would probably decompose in the

system with separation of hydroxylamine. Their effect, however, is found to be totally different from that of hydroxylamine and to be generally similar to that of the alcohols and ketones. Their strength of action, as in the case of the ketones, depends on the nature of the alkyl groups which they contain, and it may be said generally that the conversion of a ketone into the acetoxime does not cause any marked change in its physiological action.

H. C.

Physiological Action of Sulphonal. By W. J. Smith (*Zeit. physiol. Chem.*, **17**, 1—7).—Large doses of sulphonal do not influence the excretion of urinary nitrogen. There is also no effect on the sulphuric acid. Kast (*Berlin. klin. Woch.*, 1888, No. 16) states that the greater part of the sulphonal given does not enter the urine unchanged, but as a readily soluble organic sulphur compound. It was found, however, in the present research, that in dogs, after 3-gram doses in solution, small quantities of unchanged sulphonal passed into the urine. Jaffé (*Deutsch. med. Woch.*, 1891, No. 21) and Jolles (*Pharm. Post*, 1891, No. 52) have also found the same in human urine.

What are the compounds in which the greater part of the sulphonal passes into the urine? There are two possibilities: it is either *ethylsulphonic acid*, formed from the easily oxidisable ethylsulphinic acid ($HSO_2 \cdot C_2H_5$); or *sulphoacetic acid* ($SO_3H \cdot CH_2 \cdot COOH$). In order to settle the matter, these two compounds were given to dogs and men, and the urine examined.

After doses of 6 grams of potassium ethylsulphonate, the sulphuric acid was not increased, and the salt given was separated from the urine, although in too impure a form for analysis.

The same dose of sodium sulphoacetate lessened rather than increased the urinary sulphuric acid, although the total sulphur in the urine was double, showing that the salt had been absorbed. The barium salt was crystallised from the urine. In urine, after the use of sulphonal, however, no trace of barium sulphoacetate was obtainable; the chief end product of the sulphonal thus appears to be ethylsulphonic acid.

W. D. H.

Toxic Action of Carbon Bisulphide. By A. Westberg (*Zeit. anal. Chem.*, **31**, 484—486).—See this vol., p. 1520.

Chemistry of Vegetable Physiology and Agriculture.

To what extent is Atmospheric Nitrogen Assimilable? By B. Frank (*Ann. Agron.*, **18**, 414—416; from *Deut. landw. Presse*, 1891, 779).—The results of a new series of pot cultures, in which leguminous and other plants were grown, with and without nitrogenous manures, and with and without inoculation of the soil with the nodules of symbiosis in the case of the leguminous plants, may be summed up thus:—When the organism of symbiosis is absent, yellow

lupins and peas may still develop completely if supplied with nitrogenous manure, but, under the influence of symbiosis alone, better development is attained than with the nitrogenous manure in the absence of symbiosis. In the presence of symbiosis, nitrogenous manure seems even injurious to the yellow lupin, but the pea profits by an addition of nitrogenous manure, even when symbiotic growth takes place.

It has been shown that peas and yellow lupins may, in good soil, directly assimilate atmospheric nitrogen without any development of tubercles; this assimilation of nitrogen, however, is inferior to what takes place in poor soils almost entirely under the influence of symbiotic growth. Peas assimilate considerable quantities of atmospheric nitrogen in good soils, and symbiosis increases this faculty. Clover behaves like peas.

Not only does Frank hold that these leguminous plants *may* assimilate free nitrogen without the development of any root tubercles, but he has also obtained fixation of nitrogen, although to a less extent, with cultures of oats, buckwheat, spinney, asparagus, and colza, which never show any development of root nodules. J. M. H. M.

Fixation of Free Nitrogen during Vegetation. By E. Breal (*Ann. Agron.*, **18**, 369—379).—The author has grown plants of cress in river sand, watered with a solution of potassium chloride with calcium phosphate in suspension and a little added magnesium sulphate, under conditions which demonstrate the fixation of atmospheric nitrogen by the combination. A growth of four months in 6·3 kilos. of the soil showed gains of nitrogen in the aërial parts of the plants of 0·305 and 0·290 gram, and in the soil and roots of each pot of 0·339 gram N. The seeds of the plants grown in this way were lighter, and contained less nitrogenous matter than the seeds sown, which, of course, had been grown in a nitrogenous soil.

J. M. H. M.

Sodium as a Plant Food. By A. Atterberg (*Expt. Stat. Record*, **3**, 554; from *Deut. landw. Presse*, 1891, 1035).—In the author's experiments, black Tartar oats were grown in quartz sand and watered with nutritive solutions containing hydrogen potassium phosphate, magnesium sulphate, and potassium, sodium, and calcium nitrates. Different amounts of potassium were replaced by equivalent amounts of sodium and of calcium respectively. The results show a falling off in the yield of oats when the supply of potassium was diminished, but the falling off was much less in the sodium series than in the calcium series. Thus, with 9·42 grams of potassium, the sodium series gave 141, and the calcium series 142, grams of oats; with 5·65 grams of potassium, the sodium series gave 134, the calcium series 112 grams of oats; with 1·88 grams of potassium, the yields were 112 and 75 grams respectively. Sodium may thus be of great importance where potassium is deficient, and the large amount of sodium in many of the Stassfurt salts is no longer to be considered as useless. N. H. M.

Distribution and Condition of Iron in Barley. By P. Petit (*Compt. rend.*, **115**, 246—248).—When barley is treated repeatedly with a dilute solution of hydrochloric acid in alcohol, only a minute quantity of iron is dissolved, and it follows that practically the whole of the iron is present in the form of nucleïn. An investigation of the distribution of the iron in various parts of the grain shows that the dry embryon contains 0·11 per cent., the integument 0·097, and the proteïds 0·002 per cent.

During germination, the quantity of iron present in the form of nucleïn varies but little, although the proportion of iron diminishes. In the early stages of germination, the iron in the embryon is sufficient for the requirements of the plant, and none is withdrawn from the integument or the proteïds. C. H. B.

Oil of Cinnamon. By J. Weber (*Arch. Pharm.*, **230**, 232—248).—The author has examined the oil from the leaves of *Cinnamomum ceylanicum*, Breyn., and substantially confirms the results of Stenhouse (*Annalen*, **95**, 103) and Schaer (Abstr., 1882, 1300). The oil was obtained through Schuchardt, of Görlitz, from Port Louis, Seychelles Islands, and was guaranteed pure. It had the colour and odour of oil of cloves and a burning taste; its sp. gr. was 1·0552 at 18·5°. For the most part it consisted of eugenol, but contained, in addition, small quantities of cinnamaldehyde and of terpenes. Attempts to identify pinene and cineole among the latter were unsuccessful. Benzoic acid, also, could not be detected.

Another oil was examined, purporting to be obtained from the roots of the same plant, and procured from Schimmel, of Leipsic. Since the completion of the research, however, this firm have thrown doubts on the genuineness of this oil, suspecting it to be derived from the leaves. It had the colour and odour of oil of cloves, and its sp. gr. at 19° was 1·0411. This oil also consisted mainly of eugenol, but contained also safrole, small quantities of benzaldehyde, and a considerably larger amount of terpenes than the first oil examined.

C. F. B.

A Crystalline Constituent of Genipa brasiliensis, Mart. By W. Kwasnik (*Chem. Zeit.*, **16**, 109—110).—The fresh, crushed leaves are extracted three times with alcohol (sp. gr. 0·815) at 60°, the extract filtered, and the alcohol distilled completely. The residue is extracted with hot water, the solution filtered, and lead acetate added to the filtrate so long as it produces a precipitate. Another filtration and a similar treatment with tribasic lead acetate follow, and the solution is then treated with hydrogen sulphide to remove excess of lead, and evaporated to a syrup; this crystallises on cooling, and the crystals are purified by trituration with absolute alcohol and recrystallisation therefrom. Water may be substituted for alcohol in this prescription, but the yield (0·3 per cent.) is not so good. By the alcohol treatment, 0·54 per cent. was obtained from the fresh leaves, and 0·79 per cent. from the fresh bark.

The crystals are colourless, slender, sweet needles, and are insoluble in ether, light petroleum, benzene, cold alcohol, and amyl alcohol, but dissolve in water, chloroform, aniline, boiling alcohol, and acidified

amyl alcohol. The substance melts at 165°, and does not behave as a glucoside. Its empirical formula is $C_3H_7O_3$, which, together with the above properties, indicates that it is identical with mannitol. Its aqueous solution is optically inactive, except when alkalis or boric acid are present, and reduces Fehling's solution slightly after boiling or long standing. These properties are also shared by mannitol, although it is generally stated that this sugar does not reduce Fehling's solution; this may be true of it *quâ* mannitol, but an alteration product is evidently formed when it is heated with alkalis. This matter is being investigated. A. G. B.

Chemical Study of the Cotton Plant. Feeding Value of the Cotton Plant and its Parts. By J. B. McBryde (*Expt. Stat. Record*, **3**, 537—542; from *Tennessee Stat. Bull.*, **4**, 120—125, and 141—145). —The first paper includes analyses of the whole plant and of its parts, a determination of the relative weight of the different parts of the plant, and a comparison of the fertilising constituents in 1 acre of cotton (300 lbs. of lint), of corn (20 bushels), and of oats (30 bushels of grain). In the second paper, analyses with reference to food constituents are given, and the composition of the plant after picking, compared with that of oats. Analyses of the parts of cotton seed are also given.

The first table shows the percentage composition of the substances dried at 100°.

	Whole plant.	Lint.	Seed.	Bolls.	Leaves.	Stems.	Roots.
Crude ash	6·27	1·77	3·53	8·33	15·93	4·54	3·60
„ cellulose	33·40	89·75	24·13	36·90	11·26	50·18	52·39
„ fat	4·23	0·65	23·26	1·57	7·31	0·90	2·35
„ proteïn	9·85	1·61	20·61	7·84	16·89	5·45	4·39
Nitrogen-free extract	46·25	6·22	28·47	45·36	48·61	38·93	37·27

	P_2O_5.	K_2O.	Na_2O.	CaO.	MgO.	SO_3.	Insoluble.
Whole plant	7·55	22·79	1·82	24·38	8·90	3·43	7·48
Lint. 1	4·41	42·47	1·76	10·36	7·41	5·71	1·56
Lint. 2	2·94	47·10	1·51	8·30	8·96	5·01	1·56
Seeds	31·01	35·50	0·57	5·68	15·19	3·90	0·69
Bolls. 1	5·25	37·93	0·59	14·28	3·81	7·30	3·52
Bolls. 2	2·43	45·90	0·64	11·03	2·97	4·48	4·34
Leaves 1	2·78	5·04	2 22	43·13	7·68	5·13	5·65
Leaves 2	3·50	11·01	1·71	33·99	6·32	3·12	10·04
Stems. 1	5·01	23·32	2·69	26·87	10·98	3·57	1·76
Stems. 2	4·10	34·35	2·14	14·72	7·10	1·95	4·11
Roots. 1	5·10	26·00	4·88	21·04	10·16	3·82	6·19
Roots. 2	4·02	39·94	3·97	11·49	8·97	2·97	6·92

In the second table, the composition of the ash of the whole plant, and of the various parts of the plant grown in (1) 1889 and (2) 1890, are given. N. H. M.

Composition of the Ramie Plant (Boehmeria). By M. E. Jaffa (*Expt. Stat. Record*, **3**, 371—373; from *California Stat. Bull.*, **94**, 1—6).—Separate analyses were made (I) of the entire plant, (II) stalks, (III) bark, and (IV) leaves. The following percentage amounts of dry matter, ash, and nitrogen were found in the fresh substance:—

	Dry matter.	Ash.	Nitrogen.
Whole plant	18·74	1·49	0·258
Stalks (without bark)	18·25	0·57	0·146
Bark (with fibre and gum) ..	19·09	0·31	0·210
Leaves	19·35	3·81	0·481

The percentage composition of the ash of the whole plant and its parts was:—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3, Al_2O_3.	MnO.	P_2O_5.	SO_3.	SiO_2.	Cl.
I.	11·82	2·35	30·87	7·89	2·41	0·17	7·29	2·26	33·01	2·43
II.	37·79	8·15	17·32	10·58	2·95	0·35	16·38	3·46	1·56	1·87
III.	32·58	8·77	22·28	11·64	0·84	0·18	12·64	3·68	5·24	2·75
IV.	4·18	0·54	34·74	7·02	2·35	0·12	4·72	1·88	42·42	2·55

A good soil will yield about 10 tons of dried stalks and 4·25 tons of leaves per acre per annum, and thus remove about 658 lbs. of lime, 252 lbs. of potash, 156 lbs. of phosphoric acid, and 370 lbs. of nitrogen per acre. The bark and fibre, however, which is all that is wanted, contain less than 10 per cent. of the potash, 3 per cent. of the lime, 7 per cent. of the phosphoric acid, and 15 per cent. of the total nitrogen, so that the loss will be comparatively small if the leaves and stalks are returned to the soil. N. H. M.

Analysis of California Oranges and Lemons. By G. E. Colby and H. L. Dyer (*Expt. Stat. Record*, **3**, 78—81; from *California Stat. Bull.*, **93**, 1891).—The original paper gives analyses of 23 samples of oranges and 4 of lemons. The average percentage composition of the pure ash of the oranges and lemons, which amounted to 0·432 and 0·526 per cent. respectively in the fresh fruit, is as follows:—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3 and Al_2O_3.	MnO_2.
Oranges..	48·94	2·50	22·71	5·34	0·97	0·37
Lemons ..	48·26	1·76	29·87	4·40	0·43	0·28

	P_2O_5.	SO_3.	SiO_2.	Cl.
Oranges....	12·37	5·25	0·65	0·92
Lemons	11·09	2·84	0·66	0·39

N. H. M.

Food Value of Brushwood. By A. Stutzer (*Expl. Stat. Record*, **3**, 493; from *Deut. landw. Presse*, 1891, 943).—It has been proposed

to use the younger twigs from trimming out the tops of trees to supplement the food supply when crops are poor. It has to be broken up, malt (1 per cent.) added, and the whole treated with hot distillery liquid, and kept for 1—3 days. Samples so prepared from various kinds of wood had the following percentage composition:—

	Water.	Crude proteïn.	Amides and digestible proteïds.	Undigestible proteïn.	Coefficient of digestibility of crude proteïn.
Beach....	10·12	4·50	1·25	3·25	27·80
Pine	7·51	5·19	2·13	3·06	40·90
Alder....	6·87	7·12	3·56	3·56	50·00
Locust...	6·98	7·94	5·06	2·88	63·80

N. H. M.

Composition of Frozen and Unfrozen Beet-chips. By A. Stutzer (*Expt. Stat. Record*, **3**, 498; from *Deut. landw. Presse*, 1891, 943).—Samples of unfrozen and of severely frozen sugar-beet diffusion chips, taken from the same silo, contained respectively 90·4 per cent. of water and 0·6 per cent of ash, and 87·5 per cent. of water and 1·2 per cent. of ash. The percentage composition of the dried materials freed from ash was as follows:—

	Crude fat.	Crude proteïn.	Crude cellulose.	Nitrogen-free extract.	Acid.
Unfrozen	0·77	12·06	28·90	56·96	1·31
Frozen.....	1·35	10·45	18·19	65·44	4·57

The coefficient of digestibility of the proteïn was: unfrozen chips, 86·3 per cent.; frozen chips, 70 per cent. The freezing made a part of the cellulose more digestible, increased the acid, diminished the digestibility of the proteïds, and gave rise to greater losses of organic matter when kept. To prevent loss, the chips should be dried at the factory before being disposed of to farmers.

N. H. M.

New Experiments on Soil Inoculation. By Schmitter (*Expt. Stat. Record*, **3**, 491; from *Wochenschr. pomm. ökon. Ges.*, 1891, 251; compare *Bied. Centr.*, **19**, 393).—Three plots of land (size not given) which had remained long uncultivated and were free from leguminous growth, were each divided into two parts, and half of each manured with superphosphate and potassium and magnesium sulphates. The plots were then divided crosswise into eight strips (1 m. wide), being separated from each other by intervening strips, and sown with yellow lupins. Strips 2, 4, 6, and 8 of each plot were treated with fresh lupin soil (1800 lbs. to 9 tons per acre). For two months, the growth was rather weak on all the plots, but afterwards became more luxuriant. On plots 1 and 2, the growth seemed equal on all the strips up to harvest time. On plot 3, the growth remained equal on all the strips until about the middle of July, when the inoculated strips began to gain; and it was found, at the time of taking up, that the roots of the plants in these plots had more and better-developed nodules than those of the plots which were not inoculated; the length of root and the growth generally were also increased by the inoculation. In the case of plots 1 and 2, the inoculation was without effect, the number of nodules averaging the same for all the strips. The total yield of hay

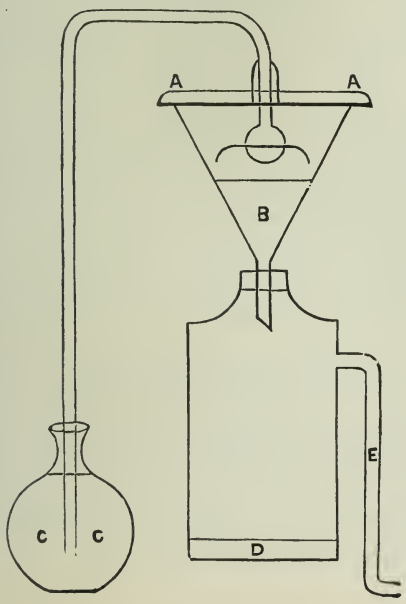
from the inoculated strips (of plot 3) was 19·188 kilos., that of the uninoculated strips 16·400 kilos.; the yields of seeds were respectively 11·200 and 10·100 kilos. N. H. M.

Inorganic Acid Substance in Soils. By P. de Mondesir (*Compt. rend.* **115**, 316—318).—A considerable proportion of the lime in soils is not combined with carbonic acid or other ordinary acid, as the amount extracted by dilute hydrochloric or nitric acids is in excess of that required to saturate the carbonic, phosphoric acids, &c., removed at the same time. The extracted soil, moreover, is still acid in reaction after washing with water, and is capable of taking up an amount of lime corresponding with the excess. The acid substance, the amount of which varies from 0·2 to 1 per cent. by weight of the soil, is not organic, for it withstands the action of moderately hot permanganate or incineration at a dull red heat, and it is not free silica, as its acid properties are not destroyed by heating for several hours at 160—170°. It resides chiefly in the clay, but not entirely, as a considerable proportion remains adhering to the sand after the clay has been separated. Neither sandstone nor kaolin shows this acidity, and colloïdal clay shows only a trace. The substance is probably an argillaceous silicate, but its nature is at present under investigation.

Jn. W.

Analytical Chemistry.

Apparatus for Washing Precipitates. By M. Forbes (*Chem. News*, **66**, 55).—The filtering funnel B is furnished with a tight-



fitting cover made of a lead and a rubber disc, A, with a bulb tube passing through the centre, and held in position by a piece of rubber tubing passing over a tubular projection on the lead disc; a long tube dipping over into the washing liquid, C, is also attached to this piece of tubing. When a precipitate is collected in the funnel, and the filter pump started, the cover, &c., are adjusted, and a steady stream of the washing liquid issues from four small holes pierced through the side of the bulb. D. A. L.

A New Combustion Furnace. By F. Fuchs (*Ber.*, **25**, 2723—2725).—The furnace, which is described with the aid of drawings, combines in principle Erlenmeyer and Babo's and Glaser's systems; the author claims to have accomplished this in such a manner that whilst the advantages of each are retained, their disadvantages are excluded. A. R. L.

Iodometry. By T. Salzer (*Zeit. anal. Chem.*, **31**, 376—381).—The author, whilst admitting with Topf (Abstr., 1887, 688) that the addition of ammonium carbonate to thiosulphate solution alters its relation to iodine, maintains that the addition has a marked effect in preserving the strength of the solution unchanged. A solution to which 2 grams of ammonium carbonate per litre had been added, proved, after keeping for five years without special precautions, to be of exactly the same strength as one freshly made without ammonia from the same specimen of thiosulphate. On the other hand, a new solution containing carbonate required a larger quantity of iodine to give a yellow colour, and this colour was not permanent until 20 per cent. more iodine had gradually been added. The addition of starch seems to prevent the disappearance of the excess of iodine, and the failure of Mohr to notice these anomalies probably arose from his use of strongly acid starch as indicator. The subject still needs investigation. The author advocates the use of chemically pure thiosulphate, and shows that the methods of testing employed by Topf (Abstr., 1887, 997) are not trustworthy. Owing to the solubility of barium sulphate and carbonate in thiosulphate solution, 2 per cent. of sodium sulphate or carbonate may be present without producing any turbidity with barium chloride. It is necessary first to oxidise the thiosulphate (together with any unsaturated sulphur salts) by a small excess of pure iodine before testing with barium nitrate. Calcium sulphide and chloride should also be looked for. A solution made from the pure salt may be accepted as a standard as long as it gives (after addition of iodine) no turbidity with barium nitrate.

M. J. S.

Detection of Chlorine and Bromine in the presence of Iodine. By D. S. Macnair (*Chem. News*, **66**, 5).—The freshly precipitated silver iodide, bromide, or chloride, or the mixture of any or all of them, is heated with potassium dichromate and concentrated sulphuric acid; by this operation the iodide is completely converted into iodate, whilst the other two salts evolve chlorine and bromine respectively, and yield silver sulphate. It only remains to identify the gas or gases evolved to complete the detection. D. A. L.

Volumetric Estimation of Soluble Sulphides. By D. Vitali (*L'Orosi*, **15**, 109—112).—This method depends on the complete precipitation of the sulphur in neutral solutions of normal sulphides by some heavy metal, phenolphthaleïn being used as an indicator to mark the finish. The solution must be free from carbonates, otherwise the carbonic anhydride must be removed by means of a soluble barium salt before proceeding; a few drops of an alcoholic solution of phenolphthaleïn are then added, and a decinormal solution of zinc acetate run in until the liquid is decolorised. Hydrosulphides may be indirectly estimated by boiling their solutions for a little while and determining the amount of normal sulphide left. In solutions containing free hydrogen sulphide, hydrosulphides, and normal sulphides, the total hydrogen sulphide may be found by titration with iodine, the solution boiled, and the normal sulphides estimated by titration with zinc acetate. If thiosulphates are also present, the amount of these must be determined in a separate portion, from which the whole of the hydrosulphide has been precipitated.

S. B. A. A.

Volumetric Estimation of Combined Sulphuric Acid. By K. Farnsteiner (*Chem. Zeit.*, **16**, 182).—The following process, originally recommended by Volhard, is, according to the author, not suitable for the estimation of large quantities of sulphuric acid, but may be recommended for the estimation of sulphates in common soda, potash, salt, and drinking water.

The hot solution, which must be faintly acidified with hydrochloric acid, is mixed with a known quantity of barium chloride. After adding pure ammonia to faint alkaline reaction, a known quantity of pure potassium chromate is added. The liquid, which should be strongly yellow, is allowed to cool, and then made up to a definite volume. One half of the liquid is now filtered, and, after acidifying with hydrochloric acid, the excess of chromate is estimated by the potassium iodide and thiosulphate method. The test analyses are satisfactory.

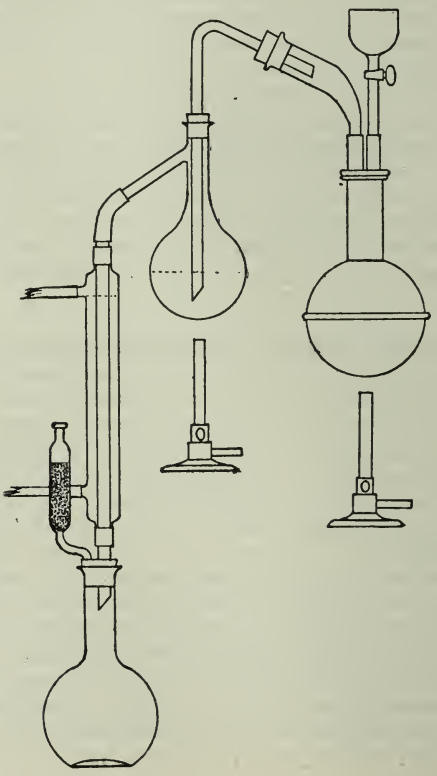
L. de K.

Estimation of Nitrogen in Organic Substances. By F. Blau (*Monatsh.*, **13**, 277—285).—The following modification of Dumas' method for the estimation of nitrogen gives a much smaller error than the original process, is more convenient for use with volatile substances and liquids, and has the further advantage of requiring only one combustion tube for a number of determinations, which can consequently be carried on in rapid succession:—The substance in which the nitrogen is to be estimated is weighed out in a small boat, placed in a combustion tube open at both ends, and gradually carbonised in a stream of carbonic anhydride. The vapours evolved are led through coarsely powdered copper oxide, the remaining carbonaceous matter is burnt in a current of oxygen, and the excess of the latter is absorbed by heated copper, which is also contained in the tube. Any nitrogen remaining in the apparatus is driven into the measuring vessel by a stream of carbonic anhydride. The apparatus is designed in such a way that oxygen and carbonic anhydride, free from nitrogen, can be passed, at pleasure, along the combustion

tube. The oxygen may be conveniently prepared by allowing commercial hydrogen peroxide (3—5 per cent.), which has been previously acidified with dilute sulphuric acid (15 per cent.), to fall on crystals of potassium dichromate contained in a specially arranged vessel. G. T. M.

Estimation of Nitrogen in Organic Substances. By W. F. K. Stock (*Analyst*, **17**, 109—112, 152—153).—The process to be described must not be considered to be a mere modification of Kjeldahl's method. In the latter process, the substance is oxidised, and its nitrogen converted into ammonia, by the sole action of boiling sulphuric acid, and only in the last stage a little potassium permanganate is added, and even this addition is not advisable. The author oxidises the substance with a mixture of sulphuric acid and manganic dioxide, and so succeeds in completely converting its nitrogen into ammonia.

From $\frac{1}{2}$ to 1 gram of the substance is mixed in a conical flask or small beaker with 10 c.c. of sulphuric acid (sp. gr. 1·84) and 5 grams of pyrolusite, which should be fine enough, but yet not too fine. The flask is heated until the contents assume a dark-green colour, which



indicates the end of the reaction. After cooling, water is added, and the contents transferred to the apparatus. An excess of sodium hydroxide is added, and the ammonia is distilled off and titrated in the usual way.

The apparatus, shown in the accompanying figure, consists of a copper boiler of 600 c.c. capacity, closed by a screw cap and india-rubber washer. This cap carries a tapped funnel for the introduction of the soda solution, and a wide evolution tube to serve as a reflux tube, in case of sudden frothing. The tube is closed by an indiarubber stopper carrying a tube bent at such an angle as to permit of its passing down the centre of a Wurtz flask, which serves as a washing flask for the vapours from the copper boiler. Both boiler and flask are provided with burners, and both must be kept boiling throughout the experiment. The Wurtz flask is in turn connected with a 14-in. Liebig's condenser, set vertically, and this terminates in a 500 c.c. receiving flask, fitted with a guard tube filled with beads, through which the standard acid is run into the receiver. The open ends of the tubes are all ground off at an acute angle, so as to prevent the formation of piston drops.

The object of the Wurtz flask is to prevent any sodium hydroxide from getting into the standard acid, and addition of zinc is quite unnecessary when using the apparatus.

In Kjeldahl's original process the oxidation generally lasts an hour; by the author's method the nitrogen is fully converted into ammonia in a few minutes.

If the substance contains chlorine, it should be first heated for some time with sulphuric acid alone before adding the manganic dioxide.

To prove the accuracy of the process, the author communicates some very successful experiments with ammonium chloride, ammonium oxalate, and potassium ferrocyanide; also experiments with bone-meal, cotton cake, and fish flesh, the nitrogen of which had been previously estimated by a soda-lime combustion. L. DE K.

Boyer's Method of Estimating Nitrogen. By C. ARNOLD and K. WEDEMEYER (*Zeit. anal. Chem.*, **31**, 388—389).—The authors have tested Boyer's method (this vol., p. 237) with various nitrates. The results showed no constant relation whatever to the calculated percentages, and no modification of the method, or of those of Ruffle and Tamm-Guyard, gave any better numbers. M. J. S.

Estimation of Nitrogen in Nitrates. By C. ARNOLD and K. WEDEMEYER (*Zeit. anal. Chem.*, **31**, 389—392).—The total nitrogen in a great variety of organic and inorganic nitrates is completely converted into ammonia by heating with a mixture of equal parts of sodium formate, soda-lime, and crystallised sodium thiosulphate with 2 parts of dehydrated thiosulphate. The operation is performed in a combustion tube 45 cm. long and 10—12 mm. bore. There is first introduced 5 cm. of a mixture of 1 part of sodium formate with 9 parts of soda-lime, then the substance with the above mixture, occupying 25—28 cm., then 10 cm. of the mixture of soda-lime and formate.

The mixtures are coarsely powdered, and the tube is tapped whilst filling so that no channel is left. The anterior layer may be rapidly heated. The only precautions required during the combustion are to avoid too tumultuous an evolution of gas, to cool well the vessel in which the ammonia is absorbed by acid, and to continue heating the tube until the last trace of water has distilled over, which requires about as long (25 minutes) as the combustion itself. For the titration, fluorescein or lacmoid is used, in order that the hydrogen sulphide present may have no influence. This method cannot be used for nitro-compounds, for nitrites, or for the nitrates of pyridine and chinoline. M. J. S.

Action of the Copper-Iron Couple on Nitrates and Nitrites in Sulphuric and Hydrochloric Acid Solutions. By K. Ulsch (*Zeit. anal. Chem.*, **31**, 392—404).—The author has now ascertained that his method for estimating nitric acid (Abstr., 1891, 960) can be simplified by working at ordinary temperatures. Iron alone reduces nitric acid in the cold very slowly and imperfectly, but when coated with copper, its reducing action is complete and rapid. Nitrites, and even a solution of nitric oxide in a ferrous salt, are similarly reduced to ammonia. 1 mol. of a nitrite ($M'NO_2$) causes a deficit of 8 atoms of hydrogen, and it is remarkable that whereas in estimating nitrates the presence of chlorides in any considerable quantity causes the reduction to be incomplete, with nitrites the results are perfectly correct even when hydrochloric acid alone is used. The injurious effect of the presence of chlorides on the nitric acid estimation can, however, be completely got rid of by adding some copper sulphate to the mixture of acid and nitrate which is to be introduced into the reaction flask, and warming to 60°. In this shape the method is suitable for the estimation of nitrates and nitrites in natural waters without the removal of chlorides.

The whole operation is carried out as follows:—The liquid containing the nitrates and nitrites is mixed with 10 c.c. of normal sulphuric acid and 10 c.c. of a 10 per cent. solution of crystallised copper sulphate, and is made up to 100 c.c.; 20 c.c. of this serves for each determination. The reaction flask is charged with 3 grams of iron powder, and the air is expelled by adding 10 c.c. of a 3 per cent. sulphuric acid. The flask is then connected with the azotometer, 2 c.c. more of the acid is run in, and then rinsed in by two additions (5 c.c. each) of the mixture to be assayed. The flask is plunged for two minutes into a water-bath at 60°, and is then shaken vigorously for two minutes. The solution is then drawn off and the flask cooled, and all is ready for the estimation. 20 c.c. of the above mixture is run in. Nitrites reveal their presence by producing the black solution of nitric oxide. The flask is shaken in the cold until this black colour just disappears. It is then warmed to 60° and shaken again. The deficit in the volume of hydrogen evolved is the sum of the deficits due to the nitrate and nitrite present. If it be wished to know the amount of each separately, the nitrite must be estimated by other means. M. J. S.

Estimation of Phosphoric Acid by the Molybdate Process. By O. Foerster (*Chem. Zeit.*, **16**, 109).—The precipitated phosphomolybdate is seldom quite soluble in ammonia, but a turbid liquid is obtained which refuses to give a clear filtrate. On adding magnesium mixture, the triple phosphate separates as a bulky precipitate, and the filtrate will be quite clear.

The magnesium precipitate is, as is well known, very difficult to wash free from adhering molybdate, which afterwards slightly increases the weight of the magnesium pyrophosphate. The precipitate will, however, be perfectly pure if the solution is gently heated before adding the magnesium mixture, but it must, of course, be allowed to cool, and be well stirred before filtering; the filtrate will be slightly turbid. The author washes with a solution containing 2·5 per cent. of ammonia and 5 per cent. of ammonium nitrate. As the molybdate chiefly sticks to the edges of the filter, these must be well washed.

L. de K.

Volumetric Estimation of Arsenic Acid. By G. Franceschi (*L'Orosi*, **15**, 192—194).—This method consists in the precipitation of the arsenate by ferric chloride, excess of ferric salt being indicated by potassium thiocyanate. The solution of the arsenate should be neutral and moderately concentrated (sodium acetate must not be used for neutralising), a small quantity of a dilute solution of potassium thiocyanate is added, and a decinormal solution of ferric chloride run in, until the blood-red coloration persists, after repeated agitation. Insoluble arsenates are first decomposed with sodium carbonate, and the product exhausted with water, neutralised with hydrogen chloride, and titrated. In presence of phosphates, satisfactory results may be obtained by first reducing the arsenate to arsenite, precipitating with hydrogen sulphide, oxidising the sulphide with nitric acid, and titrating.

Ferric salts may conversely be titrated with an arsenate, the end of the reaction being marked by the decolorisation of the thiocyanate; in the presence of salts of the alkaline earths, a solution of monopotassium arsenate should be employed.

S. B. A. A.

Separation of Thioarsenic and Thioxyarsenic Acids. By L. W. McCay (*Zeit. anal. Chem.*, **31**, 372—375).—The addition of an acid to thioarsenates causes the precipitation of arsenic pentasulphide; but highly dilute, ice-cold solutions of the thioxyarsenates (M'_3AsO_3S) remain clear for some hours when feebly acidified with hydrochloric or sulphuric acid. The mixture of alkali salts is, therefore, dissolved in about 4000 parts of ice-cold water, and a small excess of sulphuric acid is added. The flask is plunged into a freezing mixture, and a tumultuous current of air is driven through the liquid for 15 minutes to expel the hydrogen sulphide liberated by the action of the acid on the thioarsenate. The precipitate is allowed to subside, rapidly filtered off by suction, in a Gooch crucible, and washed with water, followed by alcohol. After drying at 105—110°, it is washed six or eight times with carbon bisulphide, then with absolute alcohol, and is finally dried and weighed. The cold, clear filtrate is treated with chlorine, then concentrated, and transferred to a strong bottle of

200 c.c. capacity. A vigorous stream of hydrogen sulphide is passed through until the liquid becomes opalescent; the bottle is then stoppered, and heated for an hour in boiling water. The precipitated pentasulphide is collected and washed, first with water, and then thoroughly with absolute alcohol, to remove traces of sulphur, dried at 105—110°, and weighed. The process was tested with mixtures of Bouquet and Cloëz's potassium thioxyarsenate, H_2KAsO_3S, and a sodium thioarsenate of the composition $2Na_3AsS_4,15H_2O$, and the results agreed closely with the theory. M. J. S.

Toxic Action and Detection of Carbon Bisulphide. By A. Westberg (*Zeit. anal. Chem.*, **31**, 484—486).—The action of carbon bisulphide on the blood consists in the formation of methæmoglobin, with disintegration of the corpuscles. The action of xanthic acid is due solely to the carbon bisulphide liberated by its decomposition in the body.

In cases of poisoning by carbon bisulphide, that substance can be detected in the blood. About 12—15 c.c. of the blood is drawn directly from a vein into a flask, where it is mixed with half its volume of water, and distilled under reduced pressure in a stream of carbonic anhydride or hydrogen. The carbon bisulphide can be recognised in the distillate by treatment with an ethereal solution of triethylphosphine. This reagent will detect as little as 0·54 milligram of the bisulphide. By converting the bisulphide into potassium xanthate, evaporating to dryness in a vacuum, and testing the residue with sulphuric acid and ammonium molybdate, a red colour is produced, with as little as 0·667 milligram. The thiocyanate reaction seems to reach its lower limit at 1·05 milligrams. M. J. S.

Estimation of Calcium and Magnesium in Guncotton. By H. Schjerning (*Zeit. anal. Chem.*, **31**, 283—285).—The estimation of the ash and alkalinity of limed guncotton has usually been made by Abel's processes. In 1887, the practice was commenced of adding magnesia, with or without lime, in order to obtain greater alkalinity without increase of total ash. The author has employed the following process for the estimation of these alkaline earths:—About 5 grams of the guncotton weighed in a roomy platinum crucible is moistened with a mixture of equal volumes of alcohol and ether, which, after having been saturated with paraffin and filtered, has been mixed with one-fourth of its volume of water. Some fragments of solid paraffin are added, and the ether is set on fire. The obliquely placed crucible is rotated so that the guncotton may absorb the paraffin uniformly. The partially charred residue is then rubbed down with a rounded glass rod, and the crucible is covered and heated for 15—30 minutes over the blowpipe, occasionally removing the lid. The ash is weighed, then washed out into a porcelain basin, and heated to 90° with a measured excess of N/10 hydrochloric acid. The lime and magnesia dissolve along with traces of ferric oxide and alumina sufficiently large to interfere with the direct titration of the excess of acid. A little ammonium chloride and a drop of litmus tincture are added, and the mixture is made alkaline with N/10 soda.

The resulting precipitate, with the undissolved residue, consisting of ferric oxide, alumina, and silica, is filtered off, ignited, and weighed as "impurities." The alkali in the filtrate and washings is titrated with litmus and N/10 acid. The results are obtained by the formulæ:—

$$[0{\cdot}0028\,A - (B - C)] \times 2{\cdot}5 = \text{percentage of magnesia,}$$
$$[(B - C) - 0{\cdot}002\,A] \times 3{\cdot}5 = \text{percentage of lime,}$$

where A is the number of c.c. of N/10 acid consumed by 100 grams of the guncotton, B is the percentage of total ash, C the percentage of "impurities."

The following results are communicated: they seem to relate to a single specimen, although such is not clearly stated:—

	Ash.	MgO.	CaO.	Impurities.
By gravimetric methods..	2·30	1·10	0·79	0·39
By titration as above, average of 5 analyses.....	2·33	1·14	0·81	0·38

M. J. S.

Volumetric Estimation of the Metals of the Alkaline Earths and of some Heavy Metals. By D. Vitali (*L'Orosi*, **15**, 81—85).—This method depends on the complete precipitation of salts of barium, strontium, calcium, &c., by an alkaline carbonate, phenolphthaleïn being used to indicate the close of the reaction.

The neutral solution of the metallic salt is mixed with a few drops of an alcoholic solution of phenolphthaleïn, boiled to expel dissolved gases, and decinormal sodium carbonate run in until the coloration persists, even after boiling for a few seconds. Alkaline carbonates may conversely be titrated with a standard solution of barium chloride, and bicarbonates may be treated in the same way, after boiling their solutions until they are completely converted into the normal salts. Salts of silver, cadmium, manganese, lead, zinc, and magnesium may also be estimated by titration with sodium carbonate, if the precaution is taken to boil the solution well, in order to expel the carbonic anhydride liberated during the titration, and to add sodium carbonate until the coloration is persistent, even after boiling for some time. S. B. A. A.

A New Principle of Electrolytic Separation of Metals. By H. Freudenberg (*Ber.*, **25**, 2492—2493).—Le Blanc has shown (Abstr., 1891, 1405) that in a solution the amount of the electric charge is identical for one and the same ion, and that, therefore, the point of decomposition of an electrolyte may be exactly determined. As this value differs very considerably for the various metals, the author thought it probable that their separation may be brought about by employing currents of different E.M.F., and the experiments already made show that such is really the case. Thus, with a single Leclanché cell, having an E.M.F. of 1·35 volts, silver may be separated from copper and bismuth, and mercury from copper, bismuth, and arsenic. The analyses given show a very close agreement with the theoretical numbers. H. G. C.

Analysis of Galena and Lead Sulphate. By R. Benedikt (*Chem. Zeit.*, **16**, 43—44).—The author has found that both lead sulphide and lead sulphate are rapidly acted on by hydriodic acid, with formation of lead iodide; and also that this compound is readily converted into lead nitrate by the action of nitric acid.

To make an assay of galena, a known weight of the powdered ore is put into a deep porcelain capsule, moistened with water, and treated with a few c.c. of hydriodic acid of sp. gr. 1·7. The dish is covered with a watch-glass, and warmed on the water-bath. After a few minutes, the mixture is evaporated to dryness, and then heated with dilute nitric acid, when the lead iodide is converted into nitrate with separation of free iodine. The free nitric acid and the iodine are removed by evaporation, and the lead is finally converted into sulphate by the usual method.

The process also answers for the analysis of impure lead sulphate, but to prevent separation of sulphur the compound is mixed with a little amorphous phosphorus suspended in water, before being treated with the hydriodic acid. The test analyses are very satisfactory. The author thinks that the process will serve to estimate silver in presence of lead, as silver iodide is not decomposed by nitric acid.

L. de K.

Quantitative Separation of Silver and Lead. By R. Benedikt and L. Gans (*Chem. Zeit.*, **16**, 181—182).—Benedikt (see preceding abstract) has suggested that advantage may be taken of the different behaviour of the iodides of silver and lead towards nitric acid for a quantitative separation of these two metals. The authors now state that such is really the case, and after many experiments recommend the following process:—The solution, which should contain about 0·5 gram of metal, is diluted to 200 c.c., and then mixed with a solution of 1 gram of potassium iodide in 10 c.c. of water. After adding 10 c.c. of pure nitric acid, previously diluted with 10 c.c. of water, the mixture is heated on the water-bath until the yellow colour of the precipitate has changed to an orange-red. The lead iodide soon dissolves, and iodine is set free, which is expelled by adding boiling water and evaporating for some time on the water-bath, water being added from time to time. The precipitate is then pure silver iodide, and, according to the authors, is best collected on a weighed glass-wool filter, and dried at 110°.

The presence of copper, cadmium, and bismuth does not interfere, but if mercury is present the silver iodide retains mercuric iodide.

If the silver is present only in small quantities, for instance, in the case of argentiferous galena and pig-lead, as much as 10 or 50 grams of the sample must be operated on. The authors dissolve the metal in a mixture of nitric and tartaric acids, dilute to 300—500 c.c., add 10 c.c. of a 10 per cent. solution of potassium iodide, which is sure to be sufficient to precipitate all the silver, and then proceed as described. The test analyses are extremely satisfactory. L. de K.

Estimation of Lead. By L. Medicus (*Ber.*, **95**, 2490—2492).—Lead may be estimated in an alkaline solution free from chlorides by precipitation as oxalate, which, after washing, is dissolved in nitric

acid and converted into lead peroxide by electrolysis. In presence of chlorides, however, the precipitation of the oxalate is incomplete, and the method is, therefore, not available for determining the amount of lead in galena after dissolving the mineral in hydrochloric acid; in this case, the lead chloride is dissolved in potash, carbonic anhydride passed through the solution for two hours, and the precipitated carbonate dissolved in nitric acid, and electrolysed. Another method is to dissolve the chloride in potash, and to pass a slow current of bromine vapour over the surface of the liquid until the lead peroxide sinks to the bottom and the supernatant liquid begins to assume a yellow colour; the lead peroxide is then filtered through asbestos in a perforated crucible. The analytical data given in the paper show that the method is capable of giving trustworthy results.

H. G. C.

Detection of Alum in Wines. By N. De Colli (*L'Orosi*, **15**, 118—120).—The following methods are stated to give satisfactory and concordant results:—

a. 100 c.c. of wine are evaporated to dryness in a porcelain dish on a sand-bath, and carefully heated until no more products of decomposition are evolved. The carbonised residue is pulverised in the dish, covered with dilute acetic acid, allowed to remain for 24 hours, boiled, filtered, evaporated to dryness, and heated until there is no further odour of acetic acid; water is then added, the mass again boiled, filtered, and ammonium chloride and ammonia added. Any alumina artificially introduced into the wine (as sulphate) is now precipitated; the aluminium tartrate naturally occurring in wine having been rendered insoluble by the incineration.

b. A definite quantity of the wine is evaporated to dryness in a platinum basin, and completely calcined, the process being hastened by the addition of ammonium nitrate. The ash is taken up with hot hydrochloric acid, filtered, the residue washed free from acid and sulphates, and the sulphates in the solution estimated. By comparison with the sulphates in the original wine, the amount of aluminium sulphate added (and decomposed by ignition) is ascertained.

S. B. A. A.

Estimation of Aluminium Phosphate. By C. Glaser (*Zeit. anal. Chem.*, **31**, 383—388).—The precipitation by ammonia of a solution containing alumina and excess of phosphoric acid gives, not the normal salt $AlPO_4$, but a basic aluminium phosphate. The same is the case when the precipitation is made with sodium acetate at 100°; but by heating to 70° only, and avoiding a higher temperature during the washing, the composition of the precipitate will agree exactly with the formula $AlPO_4$. The following modification of the usual process is therefore recommended. To the phosphate solution, which must not contain free chlorine, a drop of methyl-orange solution is added, and then ammonia, until the acid is all but neutralised. A few c.c. of ammonium acetate now change the colour to yellow. The mixture is then heated to 70°, when the iron and aluminium phosphates are completely precipitated. If calcium phosphate is present, a little of it adheres to the precipitate, which should therefore be redissolved in hydrochloric acid and precipitated as before, after

adding a little sodium phosphate. Should the original liquid contain free chlorine, ammonia and then hydrochloric acid must be added before the indicator. The precipitate is washed on the suction filter with water heated to 70°, gently ignited, and weighed. To estimate the iron in it, it is covered with pure sodium carbonate and fused for 10 minutes, using the blowpipe. The fused mass is boiled with water and filtered hot, and the ferric oxide washed well with boiling water. Hot filtration is necessary to prevent the separation of an aluminium phosphate of the composition $Al_3P_2O_7$, which is very sparingly soluble in cold soda solution. The iron oxide is dissolved and reprecipitated by ammonia before weighing. M. J. S.

Estimation of Manganese in the various kinds of Iron. By H. Rubricius (*Chem. Zeit.*, **16**, 217—218; 459).—The author now proceeds as follows (compare this vol., p. 1030):—2 grams of the sample is dissolved in the smallest possible quantity of hydrochloric acid, and, after being somewhat diluted, oxidised with nitric acid. The whole is washed into a large glass vessel and diluted to about 500 c.c. No notice need be taken of any suspended carbon. Sodium carbonate is now added until a faint, permanent precipitate is produced, but this is at once cleared by the cautious addition of a few drops of nitric acid, and the ferric hydroxide precipitated with elutriated zinc oxide, but a large excess of it should be avoided. The precipitate, which is at first somewhat gelatinous, soon becomes more granular, and readily subsides. About 2 grams of magnesium sulphate is added, the liquid is gently heated, and then at once titrated with permanganate. The author uses this solution of such a strength that 1 c.c. equals 0·000637 gram of manganese.

The test analyses are very satisfactory. The process may also be applied to the estimation of manganese in ferruginous slags and ores. L. de K.

Stability of Potassium Permanganate Solution. By B. Grützner (*Arch. Pharm.*, **230**, 321—324).—The solutions were kept in glass-stoppered bottles, tied over with parchment paper, and in flasks fitted as wash-bottles, so that the solution might be withdrawn without removing the cork. Some of these vessels were exposed to diffused daylight, whilst others were kept in the dark. After one year, a 0·1 per cent. solution was unaltered in its relation to freshly prepared N/10 oxalic acid solution in every case. After $1\frac{1}{2}$ years, the same solutions had lost 2·61 per cent. of their contents of potassium permanganate when kept in daylight, and 0·94 per cent. when kept in the dark. A 0·3 per cent. solution was unaltered in every case after $1\frac{1}{2}$ years. The author succeeded in keeping N/10 sodium thiosulphate solution for six months unchanged; for this purpose, light should be excluded.

The method suggested by Vulpius and Holdermann for determining the metallic iron in *ferrum reductum* by the action of dilute sulphuric acid in the cold is not practicable, for much oxide of iron is dissolved at the same time. The method of shaking the sample with mercuric chloride solution and titrating with potassium permanganate is preferable if sufficient mercuric chloride be employed. A. G. B.

Hamburger's Method of Estimating Small Quantities of Iron. By HUPPERT (*Zeit. physiol. Chem.*, **17**, 87—90).—This method (*ibid.*, **2**, 195; **4**, 249), which consists in the reduction of iron oxide with sulphurous acid instead of zinc, has been criticised by some, but the author finds that it is simple, and gives absolutely correct results.

W. D. H.

Detection of Nickel and Cobalt. By F. J. HAMBLY (*Chem. News*, **65**, 299).—The mixed sulphides of nickel and cobalt, obtained in the ordinary course of analysis, are dissolved in hydrochloric acid and potassium chlorate, and evaporated to dryness and redissolved; or the chlorine is boiled off and the excess of acid neutralised. The solution is treated with an excess of potassium cyanide beyond that required to dissolve the precipitate at first formed (boiling is unnecessary), then rendered alkaline with sodium hydroxide, and twice the volume of bromine-water added; on gently heating, the whole of the nickel is precipitated as nickelic hydroxide, whilst the cobalt remains in solution as potassium cobalticyanide. Both metals may be identified in the ordinary manner.

D. A. L.

Analysis of Chromite. By E. WALLER and H. T. VULTÉ (*Chem. News*, **66**, 17—18).—$\frac{1}{2}$ to 1 gram of the pulverised chromite is dropped on to and fused to complete decomposition with five or six times its weight of a molten flux, consisting of 2 parts of borax glass and 3 parts of fusion mixture, previously fused together, and coarsely pulverised. The fused mass is treated with water, the solution evaporated with ammonium nitrate until ammonia ceases to be evolved, and then taken to dryness with a few drops of nitric acid; the residue is redissolved in water containing a small quantity of nitric acid, and the solution, containing only chromates and nitrates, is treated with hydrochloric acid and sulphurous acid, of which the excess is boiled off. The solution is now neutralised with ammonia, boiled in presence of some ammonium sulphide, the precipitate redissolved in hydrochloric acid, reprecipitated as before, ignited, and weighed as chromic oxide.

D. A. L.

Estimation of Small Percentages of Gold and Silver in Base Metals, Mattes, &c. By C. WHITEHEAD (*Chem. News*, **66**, 19—20).—The following method is devised for estimating gold and silver in base ores, crude copper, zinc, mattes, &c. The material, the quantity depending on the proportion of precious metal present, is dissolved in nitric acid, diluted with water, mixed with 50 grams of lead acetate, 1 c.c. of dilute sulphuric acid added, and filtered; the precipitate, which contains any gold that may be present, is examined in the usual way. The filtrate is made up to a litre and in 500 c.c. lots, precipitated completely with a saturated solution of sodium bromide; the precipitates, after washing and drying, are run down with sodium carbonate, flour, and borax, the buttons cupelled, and the silver beads weighed separately.

D. A. L.

Volumetric Estimation of Gold. By G. Franceschi (*L'Orosi*, **15**, 112—115).—This method consists in the precipitation of gold from its solutions by stannous chloride or an alkaline stannite, excess of the reagent being indicated by the blue coloration which it produces in contact with phosphomolybdic acid.

The stannite must be freshly prepared. A decinormal solution is readily obtained by dissolving tin (7 grams) in concentrated hydrochloric acid in an atmosphere of carbonic anhydride, adding a saturated solution of Rochelle salt and a slight excess of pure sodium hydrogen carbonate, standardising with decinormal iodine solution, and diluting to the extent required. During the titration of the gold solution, a small drop is taken out at intervals, dropped on a piece of filter paper, and the periphery of the spot touched with a rod dipped into a solution of phosphomolybdic acid; a bluish coloration is produced at the point of contact if there is the slightest excess of stannite. A mixture of solutions of ferric sulphate and ferricyanide of potassium may also be used as an indicator, but the reaction is not so delicate. S. B. A. A.

Testing the Purity of Platinic Chloride. By A. F. Holleman (*Chem. Zeit.*, **16**, 35).—Platinic chloride is supposed to be fit for use as a reagent if it dissolves completely in absolute alcohol, and after ignition yields nothing to dilute nitric acid. The author, getting unsatisfactory results when engaged in potash estimations, suspected his platinic chloride, and found it to contain an appreciable amount of sulphuric acid.

As his potash solution contained traces of baryta, the potassium platinochloride got, in consequence, contaminated with more or less barium sulphate. L. de K.

Extraction of the Dissolved Gases from Water. By F. Hoppe-Seyler (*Zeit. anal. Chem.*, **31**, 367—372).—The extraction is effected by boiling the water in a vacuum, and transferring the gases to a measuring tube by a mercury pump. The apparatus consists of six glass pieces united by rubber tubes of 5 mm. bore and 5—7 mm. thickness. The first vessel, C, is a mercury reservoir; then follow in series three tubes of pipette form, C′, A, and B, of which A, of 250 to 500 c.c. capacity, is the collection vessel for the water. C′ and B are much narrower than A. All the rubber tubes connecting these vessels are closed by compression clips. The tube B is connected to the side branch of a tube D, of the form of a gas burette, of which both the side and upper limbs are furnished with good glass stopcocks. The lower end of D is joined by a rubber tube, 1 metre in length, to a tubular mercury reservoir E, whilst the upper limb is provided with a gas delivery tube leading to a mercury trough. To collect the water, A is placed in a vertical position and filled with mercury by influx from C. The upper end of A is then connected by tubing with the water supply, and the mercury is allowed to flow back into C. The water is thus transferred without contact with air. A is now placed in an oblique position; B is attached, and by alternately lowering and raising the reservoir E, with suitable manipulation of

the stopcocks, the tube B is exhausted of air and filled with mercury. The compression clips are now all opened, and the water in A is vigorously boiled, the reservoir C being at such a level that the pressure in A is 5—10 cm. below that of the atmosphere. After five minutes' boiling, the lower clip is closed, and the gas in B is pumped over into D and expelled into a tube standing in the mercury trough. The clip is again opened and the boiling repeated as long as any traces of gas are obtained. In the absence of carbonic acid, 6 to 10 repetitions are sufficient, but it seems to be impossible to expel carbonic anhydride from water completely, even with 40 boilings. The whole operation requires $\frac{3}{4}$—$1\frac{1}{2}$ hours. M. J. S.

A New Colour Standard for Natural Waters. By A. Hazen (*Amer. Chem. J.*, **14**, 300—310).—It is found that the Nesslerised ammonia standard of colour, although the best hitherto used, is objectionable on account of the change in the standard colours with slight variations in manipulation, the colours of the lower standards depending quite as much on the quantity and quality of the Nessler reagent used as on the ammonia. Further objections exist in the facts that the numbers expressing the colours are not directly proportional to the colours themselves, and that waters having colours less than that of Nesslerised distilled water find no place in its scale.

Standard colours prepared from a mixture of solutions of platinum and cobalt chlorides are recommended, as the colour of such solutions is, within wide limits, independent of acidity and temperature, and the standards are quite stable even in direct sunlight when containing a moderate amount of hydrochloric acid.

The colour of the standards can be made to match that of natural waters, allowing more accurate comparisons than are possible with Nesslerised ammonia. The figures obtained are directly proportional to the actual colours. W. T.

Volumetric Analyses by means of Potassium Ferrocyanide or Ferricyanide. By C. Luckow (*Chem. Zeit.*, **16**, 164—165; 835—838).—The author (compare this vol., p. 1129) recommends that the formula of potassium ferrocyanide should be doubled. The standard solution should therefore be made by dissolving 42·2 grams of the salt in 1 litre of water (a N/20 solution). The ferricyanide solution is made by taking 32·9 grams of potassium ferricyanide in 1 litre of water. The solutions may, if desired, be diluted to any given strength, so that, for instance, 1 c.c. will show exactly 0·005 of metal. Both solutions are best preserved in brown glass bottles, and, according to Moldenhauer, the ferrocyanide should be made alkaline to preserve it better. The general properties of the ferrocyanides and ferricyanides of the heavier metals are as follows:—They are coloured compounds, which are mostly insoluble in water, and readily deposit from saline solutions, but remain more or less suspended in pure water. Acids, particularly hydrochloric acid, slightly increase the solubility. At first no difficulty is experienced in filtering, but as soon as the attempt is being made to wash with pure water, some of them

have a tendency to pass through the filter. After prolonged drying at 60—70°, the granular precipitates form brittle masses readily crushed; the more bulky precipitates look more like dried gluten. Some precipitates may be dried at 200° without undergoing any marked decomposition; others, for instance, those precipitated from an ammoniacal solution, sensibly diminish in weight. Some ferricyanides are decomposed at 100°, whilst the manganese compound actually begins to glow at that temperature. On ignition, and repeated treatment with nitric acid, the metallic oxides are left. The action of ammonia is peculiar; some compounds dissolve without decomposition, but tin compounds gradually deposit the tin as hydroxide. Other metals, such as zinc, although their hydroxides are soluble in ammonia, are precipitated from their ammoniacal solution. The author also calls attention to the various, in some cases impossible, quantities of combined water which these compounds are supposed to contain, and recommends further investigation in this direction.

The reaction between potassium ferrocyanide and metallic solutions is not, however, always complete, and then in most cases the precipitates contain more or less undecomposed potassium or ammonium ferrocyanide. When working with ferricyanide, the reaction is generally more complete. The solutions should, therefore, always be checked with a known quantity of metallic salt; the titrations being effected under like conditions of reactions, &c. To show the necessity of this, the following results obtained by the author may be quoted:—

1. Action of potassium ferrocyanide on zinc: 1 c.c. of a N/20 solution = 0·00975 gram of zinc in acid solution, 0·0081 gram in neutral solution, and 0·13 gram in ammoniacal solution.

2. Action of potassium ferricyanide on cobalt: 1 c.c. of N/20 solution = 0·0088 gram of cobalt in neutral or acid solution, and 0·0103 gram in its ammonium carbonate solution.

Similar results were obtained with several other metals.

L. de K.

Estimation of Iodoform. By H. D. Richmond (*Analyst*, **17**, 7).—When iodoform is heated with alcoholic soda, a somewhat complex reaction takes place, but its 70 per cent. of iodine is practically converted into sodium iodide. On this fact, the author has based the following method for the testing of commercial iodoform.

About 0·15 gram of the sample is dissolved in alcohol, an excess of alcoholic soda is added, and, after about 10 minutes' digestion near the boiling point of the alcohol, the excess of spirit is evaporated. The residue is taken up with water, slightly acidified with dilute nitric acid, and again neutralised by a small quantity of calcium carbonate. The solution is then titrated with a weak standard solution of silver nitrate with potassium chromate as indicator. The method does not take more than half an hour to perform. Should the iodoform be obtained in ethereal solution, as, for example, in the estimation of acetone, the ether need not be evaporated, but can be mixed directly with the alcoholic soda. The test analyses are very satisfactory.

L. de K.

The Oxidation of Alcohol by Permanganate. By R. Benedikt and J. Neudörfer (*Chem. Zeit.*, **16**, 77—78).—Benedikt and Zsigmondy were the first to observe that ethyl alcohol, under certain conditions, is oxidised to oxalic acid by the action of alkaline permanganate.

The authors have been for some time engaged in trying to find out under what conditions the oxidation will be quantitative, so as to get a really simple and direct method for the estimation of alcohol, as this is still a desideratum. Their efforts have not as yet been attended with much success, as the largest amount of alcohol found did not exceed 64 per cent. of the whole; but as other chemists may, perhaps, be more successful, they thought it as well to call attention to the matter.

The experiments were made in much the same way as glycerol estimations are performed according to Benedikt and Zsigmondy's method, the best results being obtained when the 2 per cent. solution of the alcohol was added to the boiling alkaline permanganate.

L. de K.

Estimation of Glycerol in Wine. By G. Baumert (*Arch. Pharm.*, **230**, 324—331; compare Abstr., 1890, 426, 427).—The distillation vessel has the form of a U-tube, the wider limb of which is expanded to a pear-shaped bulb, and is connected with a Liebig's condenser. The narrower limb is surrounded by an air-bath, and is connected with an iron spiral tube, which is heated by burners and is for the admission of superheated steam. The wine (50—100 c.c.) is evaporated in a dish with precipitated calcium carbonate (1—2 grams) to about one-half, and introduced into the wide limb of the distillation flask, which is then heated until no more water condenses in the upper part. Superheated steam is now admitted, and the distillate collected in a 200 c.c. flask, to which volume it is subsequently diluted. Potassium hydroxide (10—12 grams), free from oxalate, is dissolved in the dilute distillate, and, after cooling, a cold saturated solution of potassium permanganate is added in excess. The mixture is boiled for some time and, after half an hour, a stream of sulphurous anhydride (from hydrogen sodium sulphite and sulphuric acid) is passed through it until the liquid is colourless, and all separated manganese oxides have dissolved. Acetic acid is next added, all sulphurous anhydride expelled by boiling, and the oxalic acid precipitated by calcium chloride solution. The precipitate will contain calcium sulphate, and cannot be weighed directly; it is washed with hot water, decomposed by sulphuric acid, and titrated with potassium permanganate solution. 90 parts of oxalic acid are equivalent to 92 parts of glycerol.

Planchon's method, whereby the distillate is oxidised completely by acid potassium permanganate solution, and the resulting carbonic anhydride weighed, does not yield such good results as the method described.

A. G. B.

New Test for Sugar in Urine. By G. Hoppe-Seyler (*Zeit. physiol. Chem.*, **17**, 83—86).—Baeyer (*Ber.*, **13**, 2260) has shown that indigo can be formed artificially from orthonitrophenylpropiolic acid by boiling it with alkalis, and reducing substances like dextrose.

This may be applied to the detection of sugar in urine. A $\frac{1}{2}$ per cent. solution of the acid in sodium hydroxide is the reagent used, and it keeps unchanged for months. Diabetic urine diluted 10 times gives a deep blue on boiling a small quantity with about five times its bulk of the reagent. The advantages claimed for the test are (1) a convenient reagent, (2) small quantities of urine will suffice, (3) albumin does not interfere with the reaction. W. D. H.

Improvement in the Method of Estimating Aldehydic and Ketonic Oxygen. By H. Strache (*Monatsh.*, **13**, 299—315; compare Fischer, *Ber.*, **17**, 572).—The author has previously (this vol., p. 546) described a method for the estimation of aldehydic and ketonic oxygen, in which the substance under investigation is added to an excess of phenylhydrazine, whereby a hydrazone is formed, and the excess of phenylhydrazine is afterwards determined by measuring the nitrogen evolved on treating it with hot Fehling's solution. The method is, however, liable to two sources of error; one, due to the fact that, under some conditions, Fehling's solution and phenylhydrazine may react with formation of aniline, lowering the results; the other raising them, owing to the tension caused by the presence of a variable quantity of benzene vapour in the gas. To eliminate these errors, the author has rearranged the apparatus employed in such a way that the solution of the compound under investigation is allowed to fall into the hot Fehling's solution; and he passes several drops of benzene into the measuring tube containing the nitrogen, the volume of the gas being afterwards corrected for the tension of the vapours of both water and benzene. Under such improved conditions, constant but, owing to the imperfect displacement of air, somewhat too high results are obtained. The further necessary correction was determined by conducting experiments in blank, and, after making due allowance, the results were satisfactory. Acetone and many other compounds gave numbers which accurately agreed with the calculated values, but anomalous results were obtained with benzile and benzophenone. Both of these, when alcohol was employed as a solvent, gave numbers corresponding with only half the oxygen present in the carbonyl groups of the compounds.

G. T. M.

Estimation of Thiocyanacetone. By J. Tcherniac (*Ber.*, **25**, 2621—2626).—See this vol., p. 1426.

Estimation of Hydrocyanic Acid. By G. Venturoli (*L'Orosi*, **15**, 85—88).—It is often impossible to estimate hydrogen cyanide in mixtures without previously isolating it by distillation; the following process is proposed for use in such cases:—

The solution containing the hydrogen cyanide is introduced into a flask of about 300 to 400 c.c. capacity, and a current of pure hydrogen passed into the liquid, the escaping gas being led into a decinormal solution of silver nitrate. In about an hour the whole of the hydrgen cyanide will have been carried over, and the silver remaining in solution is then titrated with potassium ferrocyanide. In the presence of metallic cyanides, dilute sulphuric or tartaric acid is introduced into

the flask before commencing the process. Cyanide of mercury must be decomposed with hydrogen sulphide, the solution acidified with tartaric acid, neutralised with freshly precipitated calcium carbonate in order to fix any ferro- or ferri-cyanides present, hydrogen is then passed in, and the issuing gases led first through a solution of bismuth nitrate to remove hydrogen sulphide, and then into the silver solution.

S. B. A. A.

Separation of Malic Acid from Succinic, Citric, and Tartaric Acids. By C. Micko (*Zeit. anal. Chem.*, **31**, 465—468; from *Zeit. allgem. österr. Apotheker-Vereins*, **30**, 151).—The solution, which must contain the acids (about 0·7 gram) as potassium salts and be feebly acid, is evaporated in a flask to about 10—15 c.c., then mixed with 0·5 gram of barium acetate and excess of baryta water, and gradually heated to boiling. The bulky precipitate is collected and washed with baryta water, but not too long, as the precipitate would begin to redissolve. The filtrate is heated nearly to boiling and treated with carbonic anhydride until nearly or quite neutral. Excess of baryta water is again added, and after 24 hours the precipitate is collected and washed as before. The excess of baryta is now removed by passing carbonic anhydride through the hot liquid, filtering, and washing with hot water. The filtrate and washings are feebly acidified with acetic acid, concentrated to 10—25 c.c., once more boiled with baryta, then treated with carbonic anhydride, and again made alkaline with baryta. On filtering after 24 hours, and washing the precipitate with baryta water, the filtrate will contain all the malic acid and be free from the other acids. The baryta is now thrown down hot with carbonic anhydride, and the acidified filtrate is concentrated and precipitated by a small excess of potassium carbonate. The filtrate is acidified, evaporated, mixed cold with an excess of acidified lead acetate (5 c.c. of 1 : 5), and then with 120 c.c. of 80 per cent. alcohol. After 48 hours, the precipitate is collected and washed, first with cold, then with hot 80 per cent. alcohol. Should the filtrate be turbid, it is boiled in a flask with reflux condenser until clear, and then set aside for 48 hours. The small precipitate is collected, and washed with cold alcohol. The lead in the two precipitates is determined, and the amount of malic acid calculated therefrom.

M. J. S.

Estimation of Tartar in Sweet Wines by the Method of Berthelot and Fleurieu. By E. Ackermann (*Zeit. anal. Chem.*, **31**, 405—407).—The author has met with a sweet Greek wine, which, like the Carlowitz examined by Petrowitsch (Abstr., 1886, 652), gave no crystalline precipitate when mixed with ether-alcohol. Petrowitsch inferred from this the absence of tartar, and assumed that the whole of it had been precipitated by the 14·65 vols. per cent. of alcohol, under the conditions of long keeping in a very cold cellar. In both cases, however, a soft, slimy, brown precipitate was obtained. In the author's case, this proved to be chiefly sugar, containing, however, tartar, the crystallisation of which was prevented by the syrup. After complete fermentation of the wine, a crystalline precipitate of tartar could be obtained, but none of the slimy matter. The limit of alcoholic strength at which a wine cannot retain tartar is, therefore,

above the 14·8 vol's. per cent. present in this specimen. Since a quantitative experiment with an artificial sweet wine showed that after complete fermentation the whole of the tartar added could be recovered, it is recommended that sweet wines should be fully fermented before precipitating with ether-alcohol.

To the assertion of Dietzsch that a wine from which no tartar can be precipitated in the course of 24 hours must be artificial, it may further be objected that genuine wines, which have been over-plastered, will have lost the whole of their tartaric acid as calcium tartrate. M. J. S.

Separation of Salicylic from Benzoic Acid. By Miss J. Schaap (*Chem. News*, **66**, 42—43).—By treating solutions containing salicylic and benzoic acids with excess of bromine, the former is wholly precipitated as the dibromo-derivative, whilst the benzoic acid remains in solution. D. A. L.

Estimation of Fat in Milk. By H. Leffmann and W. Beam (*Analyst*, **17**, 83—84).—The authors proceed as follows:—15 c.c. of milk is put into a 30 c.c. bottle, the neck of which is graduated so that a volume of 1·5 c.c. is divided into 86 parts. 3 c.c. of a mixture consisting of equal parts of fusel oil and hydrochloric acid is added, and strong sulphuric acid is poured in slowly, with agitation, until the bottle is filled nearly to the neck. The liquid becomes hot, and the caseïn dissolves to a dark, reddish-brown liquid. The neck is now filled to near the zero point with a hot mixture of sulphuric acid and water, and the bottle whirled for one to two minutes in their centrifugal machine, but in the case of skimmed milks from three to four minutes are required. The volume of the fat may then be read off, each division on the neck representing 0·1 per cent. of butter-fat.

The test analyses are satisfactory.

O. Hehner (*Analyst*, **17**, 102) also obtained satisfactory results by using one of the author's machines. If the specific gravity of the sample is carefully taken, the percentage of total solids contained in the milk may be found by calculation, using Hehner's formula, or by means of Richmond's slide rule, and a milk analysis may thus be finished in a very few minutes. L. de K.

Detection of Foreign Fats in Butter. By J. Erdélyi (*Zeit. anal. Chem.*, **31**, 407—410).—Pure butter fat dissolved in three times its volume of cumene (boiling point 165° at 758 mm. bar.) gives a solution which remains clear at 0° for at least an hour, and usually for much longer, whilst mixtures of butter with margarine and with lard become turbid much earlier. The mode of procedure was to filter the fat, cool it for 24—48 hours in a refrigerator, place 2 c.c. of it with 6 c.c. of cumene in a clear, dry test-tube of 2 cm. diameter, and after 24 hours at ordinary temperature to plunge the tube into powdered ice, and, after the lapse of an hour, examine it at short intervals. Further investigation of the method is solicited. M. J. S.

Horse Fat. By C. Amthor and J. Zink (*Zeit. anal. Chem.*, **31**, 381—383).—The following numbers are mean values from two determinations. The melting points were the temperatures at which the fats became transparent in capillary tubes :—

	Kidneys.	Neck.	Flank.	Foot.
Consistence.	Soft.	Like fresh butter.	Like butter.	Semi-fluid.
Colour.	Golden yellow.	Deep orange.	Golden yellow.	Pale. yellow.
Specific gravity at 15°	0·9320	0·9330	0·9319	0·9270
Melting point	39°	34—35°	36—37°	—
Solidifying point	22°	30°	20°	—
Melting point of the fatty acids	36—37°	41—42°	39—40·5°	—
Solidifying point of fatty acids	30—30·5°	32—33°	31—32·5°	—
Hehner's number	95·47	95·42	94·78	—
Reichert's number	0·33	0·22	0·38	—
Saponification number	198·7	199·5	197·8	—
Acidity (milligrams of potassium hydroxide for 1 gram of fat)	1·73	2·44	1 84	—
Acetyl number	6·64	13·74	11 62	—
Iodine number	81·09	74·84	81 60	90·30
Iodine number for the fatty acids	83·88	74·41	83·37	—

With lapse of time, horse fat becomes more fluid, and a crystalline deposit separates from it. It also becomes nearly colourless with age (Abstr., 1889, 1076). M. J. S.

New Method for the Estimation of Unsaponifiable Matter in Fats. By W. Mansbridge (*Chem. News*, **65**, 253—255).—The ether method proving unsatisfactory for the extraction of unsaponifiable matter from wool, grease and fat, the following method has been devised by the author. After the mass has been decomposed with acid, subsequent to saponification, a convenient quantity is treated with 50 c.c. of methylated spirit saturated with light petroleum (b. p. 43°), and 50 c.c. of the light petroleum is then added; the whole is heated to boiling in a reflux apparatus, and after it has been cooled slightly, it is neutralised with a measured quantity of semi-normal potassium hydroxide, and placed in a separating funnel; if the separation is imperfect, a few c.c. of boiling alcohol is added. The petroleum layer is then separated, and washed by agitating, first with 50 c.c. of water at 38°, or with 50 per cent. alcohol, and then with 40 c.c. of 70 per cent. alcohol. The distillation is conducted, by preference, over an argand flame turned down to a blue light, and the "drying" completed by blowing in the warm flask, while it is slowly rotated. A second extraction with the light petroleum is usually found to remove practically all the unsaponifiable matter from the alcoholic soap solution. D. A. L.

New Reaction of Xanthine and Allied Compounds. By E. Drechsel (*Ber.*, **25**, 2454).—Xanthine, hypoxanthine, and guanine, like alkaline urates, form compounds with cuprous oxide. If their ammoniacal solutions are mixed with Fehling's solution, boiled, and solution of dextrose dropped in, white, flocculent precipitates of the cuprous oxide compounds are formed. Similar precipitates are formed in a cold solution if a hydroxylamine salt is added.

C. F. B.

Detection of Atropine. By L. Fabris (*Gazzetta*, **22**, i, 347—350).—A patient at a hospital in Padua, who had for some time been treated by daily injections of 6 milligrams of strychnine nitrate, died a few hours after receiving an accidental injection of 3 milligrams of normal atropine sulphate, exhibiting acute symptoms of atropine poisoning. At the *post-mortem*, the presence of bilateral mydriasis, and of congestion of the meninges and of the cerebellum became evident. On examining the viscera by the Stas-Otto method, clear indications of the presence of an alkaloïd were obtained, but on applying the special reactions for strychnine and atropine, the results were negative. To test the possibility of these alkaloïds obscuring each other's reactions, mixtures of 3 per cent. solutions (the strength of the injections) of strychnine nitrate, and atropine sulphate were tested with sulphuric acid and potassium dichromate, and by Vitali's reaction, with the following results. A mixture of equal parts of the solutions gave the strychnine reaction very clearly, but the atropine reaction not at all; a mixture of 1 of strychnine with 3 of atropine gave the strychnine reaction, but not that of atropine; a mixture of 1 part of strychnine with 4 of atropine gave indistinct reactions for both alkaloïds; a mixture of 1 of strychnine to 5 of atropine gave a momentary atropine reaction; the characteristic violet coloration is, however, immediately superseded by a reddish tint. Vitali's reaction was not clearly obtained until at least 9 parts of the atropine solution were added to 1 of strychnine. It further appeared that a solution of strychnine too dilute to give the characteristic reactions of that alkaloid may effectually obscure the atropine reaction; thus 1 drop of the 3 per cent. strychnine solution diluted with 10 drops of water scarcely yields the strychnine reaction; on adding 4 drops of atropine solution to this, no reaction for atropine could be obtained.

A piece of meat injected with 0·05 c.c. of a 3 per cent. solution of each of the alkaloïds, and extracted by the Stas-Otto process, yielded a barely sensible strychnine reaction and no trace of atropine. Finally, on injecting a mixture of 3 parts of the 3 per cent. strychnine solution and 1 part of the atropine solution into a frog, paralysis of the lower limbs and a great augmentation of the nervous sensibility ensued; on introducing the mixture into the eye of a dog, distinct mydriasis was observed in fifteen minutes. It thus appears that in cases of poisoning by atropine, the physiological evidence may be conclusive when the chemical tests yield doubtful results.

S. B. A. A.

Analysis of Coffee Substitutes. By Moscheles and R. Stelzner (*Chem. Zeit.*, **16**, 281—282).—Imitation coffee may, as a rule, be

distinguished from the real article by yielding a much higher aqueous extract. According to the author's experience, the best way of determining the amount of extract in a sample is as follows :—25 grams of the compound is rubbed in a mortar, introduced into a litre flask, and digested with about 500 c.c. of water on the water-bath for half-an-hour; the mixture is now made up to the mark with water, and allowed to cool. Some of the liquid is filtered, and 50 c.c. of the filtrate evaporated in a platinum dish, containing a known weight of dry sand. Pure coffee, when treated in this manner, gives from 20 to 30 per cent. of extract only; some coffee substitutes yield as much as 72 per cent. L. DE K.

Approximate Estimation of Adulteration of Earth-nut Cake and Meal. By L. HILTNER (*Landw. Versuchs-Stat.*, **40**, 351—355).—The substance (about 0·2 gram) is placed on an inverted plate and completely moistened with tincture of iodine. After a few minutes, the meal is distributed over the whole surface by means of a jet of water from a wash-bottle. The liquid must still contain iodine, and is made clear by the addition of a few drops of alcohol. The water is now drawn off, and the substance air dried and placed on green paper. By means of a lens of low power, the particles of cake which are blackened by the iodine are readily separated from the poppy seeds; the separated portions are then weighed. In an experiment made with known quantities, 10·64 per cent. of poppy seed was found instead of 10 per cent. In this case, the particles of the ground cake were rather large, and the separation therefore easy. When there are finely-powdered, dust-like particles, the separation is more difficult. After treatment with iodine and drying, the substance is sifted in a 0·25-mm. sieve and the separation in the coarse portion is made as usual. In two check experiments, the results were within 5 per cent. of the actual amount. The percentage of poppy seed in the portion passing through the sieve may be determined by separating under a microscope, but the amount is generally small, and may be judged without actual separation.

The method is quickly carried out, and is applicable not only in the case of adulteration with poppy seed, but in nearly every case, as the substances used for adulteration are nearly all free from starch.

N. H. M.

Analysis of Peptones. By C. W. HEATON and S. A. VASEY (*Analyst*, **17**, 28—34).—After a careful trial of all the processes at present in use, the authors have found that by a combination of several of them the analysis may be simplified. No new reagents are suggested.

It is best to work with a tolerably concentrated solution. Any portion insoluble in warm, but not boiling, water must be filtered off, and treated separately for nitrogen. If a jelly is under examination, it must be liquefied by heat or dilution. In the following scheme, a strength of about 20 per cent. of solid matter is assumed, including mineral salts. It is best to make separate estimations of water, ash, and total nitrogen.

1. *Water; Ash; Total Nitrogen.*—Estimated as usual.

2. *Albumin ; Coagulable Gelatin ; Albumose ; Peptone.*—40 grams of fluid peptone is dropped gradually into 300 c.c. of absolute alcohol, contained in a large, weighed beaker, and the mixture agitated by gentle centrifugal motion. The above-named compounds soon separate, and can be washed with alcohol by decantation. The alcoholic liquid (*stock alcoholic solution*) is kept for further investigation. The precipitate in the beaker is dried to constant weight at 100°.

(*a.*) *Albumin.*—The precipitate is digested with warm water, and washed on a tared filter. The insoluble residue represents the albumin. The filtrate is diluted to 250 c.c., and constitutes the *stock aqueous solution.*

(*b.*) *Albumose and Gelatin.*—25 c.c. of the stock aqueous solution is evaporated to a few c.c., treated with a saturated solution of ammonium sulphate, raised to nearly 100°, and quickly cooled with centrifugal agitation. The precipitate is collected on a tared filter, washed with ammonium sulphate, dried, and weighed. The adhering ammonium sulphate is estimated by means of barium chloride, and allowed for.

(*c.*) *Albumose.*—50 c.c. of the stock aqueous solution is heated to near 100°, and then treated with 30 c.c. of Stutzer's reagent (an emulsion of cupric hydroxide in dilute glycerol). The precipitate is washed on a filter with hot water, and the nitrogen contained in it estimated by the Kjeldahl method.

(*d.*) *Gelatin.*—A direct estimation may be made as follows :—The filtrate from the copper precipitate is concentrated to a few c.c., in a beaker previously weighed with a glass rod in it ; saturated solution of ammonium sulphate is then added, the mixture raised nearly to the boiling point, and then quickly cooled with centrifugal agitation. The gelatin now separates and adheres to the sides and bottom of the beaker, particularly if well manipulated with the rod. After a slight washing with iced water, it may be dried and weighed. As it contains some ammonium sulphate, this must be estimated and allowed for.

The Stock Alcoholic Solution.—This is made up to 500 c.c., and divided into fractions for separate treatment.

(*a.*) *Gelatin Soluble in Alcohol.*—100 c.c. is evaporated to dryness, taken up with warm water, and estimated, as directed, by means of ammonium sulphate.

(*b.*) *Urea, &c.*—50 c.c. is evaporated to dryness, and treated with sodium hypobromite, but the nitrogen cannot safely be calculated as urea.

(*c.*) *Nitrogen.*—100 c.c. is evaporated and treated by the Kjeldahl process. After allowing for the nitrogen present as gelatin, the difference multiplied by 3·12 gives the amount of crystallisable nitrogenous compounds calculated as creatine.

(*d.*) *Ash Soluble in Alcohol.*—Another fraction may be used for the estimation of the ash. L. DE K.

INDEX OF AUTHORS' NAMES.

ABSTRACTS. 1892.

And also to Transactions, 1892 (marked TRANS.); and to such papers as appeared in the Proceedings during the Session 1891—1892 (Nos. 101 to 114; Nov., 1891, to July, 1892), but not in Transactions (marked PROC.).

A.

Abbona, V. See Fileti.
Abbott, A. C. See Voit.
Abel, J. J., and E. Drechsel, carbamic acid, 518.
Abelous, J. E., and F. Heim, digestive ferments in crustacean eggs, 362.
Abenius, P. W., and H. G. Söderbaum, diphenyltetraketone, 69.
Abney, colour-photometry, PROC., **1891**, 150.
Abrahall, J. L. H., obituary notice of, TRANS., 486.
—— the atomic weight of boron, TRANS., 650.
Ackermann, estimation of tartar in sweet wines, 1531.
Adams, F. D., melilite-bearing rock from Canada, 1058.
Adams, M. A., estimation of oxygen dissolved in water, TRANS., 310.
Addyman, F. T., action of sulphuric acid on the bromides of potassium, sodium, and hydrogen, TRANS., 94.
Adeney, W. E., and T. A. Shegog, combination of wet and dry methods in chemical analysis, 100.
Adkins, H., relations between atomic weights, 938.
Adrian and Bougarel, separation of barium from strontium salts, 776.
Ahrens, C., derivatives of metaxylene, 1437.
Aisinmann, S. See Wildermann.
Albert-Lévy, ammonia in rain water, 381.
Aldringen, F., thiocoumarin and its analogues, 329.
Alexander, H., action of formaldehyde on orthodimethyltoluidine, 1320.
Alexander, H., reduction of coumarone, 1318.
Alexéeff, W., elaterite and dopplerite, 689.
Allard. See Leze.
Allen, A. H., assay of aconite preparations, 392.
Allen, A. H., and W. Chattaway, examination of spirits for secondary constituents, 244.
Allendorff, O., oximes of opianic and phthaldehydic acids, 180.
Altschul, J., parahydroxyalkyl derivatives of phenylhydrazine, 1198.
—— paralkyloxy-derivatives of phenylhydrazine, hydracetine, and antipyrine, 1080.
Alvisi, U., formation of pyrazole derivatives from the dichlorhydrins and tribromhydrins, 884.
—— the camphor group, 1343.
Amagat, E. H., density of liquefied gases and their saturated vapours: critical constants of carbonic anhydride, 1043.
—— determination of the density of liquefied gases and of their saturated vapours, 934.
—— new isothermal curves for carbonic anhydride, 3.
Amthor, C., and J. Zink, horse fat, 1533.
André, G., bismuthic acid, 413, 688.
André, G. See also Berthelot.
Andréeff, A. See Andres.
Andreocci, A., synthesis of 1 : 3-phenylpyrrodiazolecarboxylic acid, 3-methylpyrrodiazole, 3-pyrrodiazolecarboxylic acid, and pyrrodiazole, 636.
Andres, G., and A. Andréeff, Russian peppermint oil and menthylamine, 723.

Angeli, A., action of nitrous acid on some unsaturated aromatic compounds, 447, 1198.
—— estimation of sulphur in organic substances, 382.
—— ethyl acetothienoneoxalate, 154.
—— use of sodium hypophosphite in Sandmeyer's reaction, 305.
Angeli, A., and A. Chiussi, action of iodic acid on levulinic acid, 1179.
Angeli, A. See also Ciamician.
Ankersmit, H. J. See Pictet.
Anschütz, R., and E. Parlato, ethyl dioxysuccinate, 1181.
Antony, U., removal of platinum from iridium, 1285.
Antony, U., and A. Lucchesi, auric sulphide, 280.
Appiani, G. See Menozzi.
Araki, T., formation of sugar and lactic acid in the organism, 517, 1113.
Arata, P. N., and F. Canzoneri, "Pillijan" (*Lycopodium saururus*), 894.
Archarow, J., estimation of organic matter in the atmosphere, 542.
Arche, A. See Kornauth.
Armstrong, H. E., contributions to an international system of nomenclature: the nomenclature of cycloids, Proc., **1892**, 127.
—— note on anhydrides of sulphonic acids, Proc., **1892**, 41.
—— the interaction occurring in flames, Proc., **1892**, 22.
—— the origin of colour. II. The constitution of coloured nitro-compounds, Proc., **1892**, 101.
—— the origin of colour. III. Colour as an evidence of isodynamic change: the existence of isodynamic acids, Proc., **1892**, 103.
—— the origin of colour: note on the appearance of colour in quinoline derivatives and of fluorescence in quinine salts, Trans., 789.
Armstrong, H. E., and J. F. Briggs, the relative orienting effect of chlorine and bromine. I. The constitution of parabrom- and parachlor-anilinesulphonic acids, Proc., **1892**, 40.
Armstrong, H. E., and F. S. Kipping, camphorone, a product of the action of dehydrating agents on camphor, Proc., **1891**, 188.
—— —— the production of the ketone 1 : 2 : 4-acetylenecorthoxylene from camphor by the action of sulphuric acid and zinc chloride, Proc., **1892**, 54.
Armstrong, H. E., and E. C. Rossiter, the action of alcohols on sulphonic chlorides as a means of producing ethereal salts of sulphonic acids, Proc., **1891**, 184.
Armstrong, H. E., and E. C. Rossiter, the action of bromine on a mixture of ortho- and para-nitro-α-acenaphthalide, Proc., **1891**, 186.
—— —— the action of bromine on α- and β-bromonaphthalene, Proc., **1891**, 184.
—— —— the sulphochlorides of the isomeric dibromonaphthalenes, Proc., **1891**, 182.
Arnaud, A., new acid of the $C_nH_{2n-4}O_2$ series, 582.
Arnaud, A. See also Grimaux.
Arnold, B. See Lellmann.
Arnold, C., and K. Wedemeyer, Boyer's method of estimating nitrogen, 1517.
—— —— estimation of nitrogen in nitrates, 1517.
Arnst, T. See Zincke.
Arrhenius, S., applicability of Planck's proof of the law of Van't Hoff, 935.
—— correction in the calculation of the heat of dissociation of electrolytes, 931.
—— diffusion in aqueous solutions, 1265.
—— electrical conductivity of substances in mixed solvents, 1038.
Arsonval. See D'Arsonval.
Arthus, M., glycolysis in blood, 900.
Aschan, O., hydrobenzoic acid, 847.
Aschoff, K. See Jannasch, Mai.
Askenasy, P., and V. Meyer, nitropropylene, 1062.
—— —— photochemical notes, 939.
—— —— slow combustion of gaseous mixtures, 938.
Aslanoglou, P. L., supposed copper nitride, 409.
Atherton, T. W. T., occurrence of a natural gold sulphide, 283.
Atterberg, A., sodium as a plant food, 1508.
Aubin, E., separation and estimation of lead, silver, and zinc in galena and blende, 1378.
Aufschläger, H., formation of zinc cyanide on heating nitrogenous organic substances with zinc dust, 1164.
Autenrieth, W., and O. Hinsberg, derivatives of orthotoluylenediamine, 709.
—— —— hydroxyquinoxalines and ethoxyquinoxalines, 732.
—— —— phenacetine: metaethoxyorthophenylenediamine, 160.

Auwers, K., E. Köbner, and F. v. Meyenburg, synthesis of polybasic fatty acids, 41.
Auwers, K., and V. Meyer, Claus's theory of the benziloximes, 186.
—— —— stereoisomeric nitrogen compounds other than oximes, 598.
Auwers, K., and M. Siegfeld, benziloximes, 1470.
Aymonnet, relation between the index of refraction, density, molecular weight, and diathermanous power of a substance, 1.

B.

Babington, F. W., analysis of sugar, wine molasses, and syrup, 388.
Bach, R., thermochemistry of hydrazine. Molecular refraction of some nitrogen compounds, 933.
Bachmetéeff, P., magnetism and atomic weight, 672.
Bader, R., alkalimetric estimation of phenol, 543.
Baeyer, A. v., quinitol, the simplest sugar of the inositol group, 833.
—— reduction products of phthalic acid. Constitution of benzene, 1211.
—— synthesis of dihydrobenzene, 1074.
—— synthesis of dihydroparaxylene, 1182.
Baeyer, A. v., R. Schoder, and E. R. Besemfelder, hydronaphthoic acids, 191.
Bagard, H., thermoelectric phenomena at the contact of two electrolytes, 1037.
Bailey, E. H. S., the Tonganoxie meteorite, 284.
Bailey, G. H., and J. C. Cain, simple and rapid method of gravimetric analysis, 524.
Bailey, G. H., and T. Lamb, the atomic weight of palladium, Trans., 745.
Bailey, H., alloy of tin and sodium, 572.
Baker, H. B., action of light on silver chloride, Trans., 728.
Baker, J. L. See Ling.
Balbiano, L., platinum compounds derived from the pyrazoles, 885.
Baldracco, G. See Errera.
Balestra, E., mercurammonium compounds, 276.
Balland, aluminium, 1281.
Ballantyne, H. See Thomson.
Balli, B., estimation of cream of tartar in wine lees, 1033.
Baltzer, O. See Pechmann.
Bamberger, E., symmetrical bisphenyl hydrazone of mesoxaldehyde, 162.
Bamberger, E., and B. Berlé, benzimidazoles, 632.
Bamberger, E., B. Berlé, and L. Strasser, behaviour of carvacrol towards reducing agents, 157.
Bamberger, E., and W. Dieckmann, biguanide, 737.
—— —— synthesis of guanamine, 736.
Bamberger, E., and M. Kitschelt, action of hypochlorous acid on β-naphthaquinone, 494, 857.
—— —— preparation of isoquinoline from naphthalene, 882.
Bamberger, E., and J. Lorenzen, benzimidazoles, 631.
Bamberger, E., and L. Seeberger, synthesis of closed chains, 735.
Bamberger, M., natural resins, 204.
Barba, W. P., use of asbestos in filtration, 751.
Barbier, P., essential oil of *Licari kanali*, 1236.
—— puleone, an isomeride of camphor, 627.
Bardach, B. See Goldschmidt.
Bardy, C., detection of higher alcohols in spirits of wine, 1379.
Barral. See Lépine.
Barrows, A. E., and T. Turner, estimation of slag in wrought iron, Trans., 551.
Barsiloffsky, J., condensation of aldehydes with azo-compounds, 854.
Barth, K., complex salts of sulphurous acid, 564.
Barthe, L., strontium phosphate, 1156.
Barthe and Falières, preparation of pure strontium salts, 1277.
Barthel, G., Bunsen burner for spirit, 1386.
Bartolotti, P., action of phosphorus pentachloride on methylhydrocotoïn and methylprotocotoïn, 1314.
—— derivatives of isoapiole, 1315.
Bartoshewitsch, S. T., sulphates and ethereal hydrogen sulphates in urine during diarrhœa, 1505.
Barus, C., volume lag and its bearing on molecular constitution, 1043.
Bary, P., refractive indices of saline liquids, 929.
Basset, H., tabular expression of the periodic relations of the elements, 562.
Battandier, J. A., glaucine, 893.
Baubigny, H., estimation of thallium, 238.

Baubigny, H., and E. Péchard, efflorescence of metallic sulphates, 1271.
Bauer, M., basalt of the Stempel, near Marburg, 126.
Bauer, R. W., sugar from linseed, 1293.
—— sugar from quince juice, 128.
Baumann, A., gasvolumetric analysis, 538.
—— new methods in quantitative analysis, 103, 538.
Baumann, E., estimation of homogentisic acid in the urine, 925.
Baumann, E., and E. Fromm, thioderivatives of furfuraldehyde, 301.
Baumann, E., and M. Klett, stilbene, thionessal, and tolane sulphide, 184.
Baumert, G., estimation of glycerol in wine, 1529.
Bayrac, P. H., indothymol and thymoquinone, 1311.
Beadle, C., the acid action of drawing papers, Proc., **1892**, 34.
Beam, W. See Leffmann.
Béchamp, A., action of light on silver chloride, 775.
Beck, C. See Haeussermann.
Beck, C. R. See Shenstone.
Beck, L. See Claus.
Becker, A., reduction of nitric acid to ammonia by the galvanic current, 403.
Becker, A. See also Sachsse.
Beckmann, E., and T. Paul, action of sodium on ketones and aldehydes, 169.
Beckurts, H., anemonin, 1241.
Beckurts, H., and P. Nehring, constituents of Angostura bark, 642.
Becquerel, H., optical measurement of high temperatures, 761.
Beddies, A. See Krafft.
Béhal, A., constitution of caprylaldehyde, 293.
Béhal, A., and A. Desgrez, action of fatty acids on olefines, 1162.
—— —— action of organic acids on acetylenic hydrocarbons, 1064.
Béhal and Desvignes, asbolin, 1312.
Behrend, M. See Rung.
Behrend, R., intramolecular change of some isaldoxime derivatives, 50.
—— molecular transformation of the aldoximes, 163.
—— solubility of double compounds, 1047, 1385.
Behrend, R., and E. König, alkyl derivatives of hydroxylamine, 1456.
Behrend, R., and D. Nissen, orthochlorobenzaldoximes, 1199.
Behrens, H., formation of mixed crystals, 10.
Bein, S., estimation of fat in yolk of eggs, 1134.
Békétoff, N., heat of combination of bromine and iodine with magnesium, 762.
—— influence of steam and other gases on the combustion of carbonic oxide and oxygen, 274.
—— properties of cæsium and its hydroxide, 274.
—— reduction of cæsium, 274.
Bel. See Le Bel.
Bell, J., analysis of spirits, 387.
Benedikt, R., analysis of galena and lead sulphate, 1522.
Benedikt, R., and L. Gans, quantitative separation of silver from lead, 1522.
Benedikt, R., and J. Neudörfer, oxidation of alcohol by permanganate, 1529.
Bener, P., xanthones and hydroxyxanthones of the naphthalene series, 1099.
Bentley, W. B. See Jackson.
Berend, L., and E. Thomas, ketones of the quinoline series, 1488.
Berg, A., action of sodium and potassium cyanide on chlorodiamylamine, 804.
—— chlorine derivatives of isobutylamines, 1172.
Berghell, H. See Ramsay.
Berkenheim, A., menthol, 866.
Berkenheim, A. See also Wallach.
Berlé. B. See Bamberger.
Bernays, A. J., obituary notice of, Trans., 488.
Bernthsen, A., ammonium bases of phenylacridine, 1095.
Berthelot, new method of organic analysis, 753.
—— oxidation of nickel carbonyl, 279.
—— persulphates, 12.
—— persulphuric acid and its salts, 931.
—— use of compressed oxygen in the calorimetric bomb, 673.
Berthelot and G. André, estimation of sulphur in vegetable soils, and the forms in which it is present, 656.
—— —— fermentation of blood, 900.
—— —— spontaneous oxidation of humic acid in vegetable soil, 655.
Berthelot and Matignon, heat of formation of hydrazine and hydrazoic acid, 261.
—— —— heats of combustion and formation of ethyl alcohol and formic and acetic acids, 1139.

Berthelot and Matignon, heats of combustion and formation of nitrobenzenes, 4.
Berthelot, D., basicity of phosphoric acid, 394.
—— existence of acid or basic salts of monobasic acids in very dilute solution, 110.
—— study of the chemical neutralisation of acids and bases by means of their electrical conductivities, 2.
Bertin-Sans, H., and G. Moitessier, formation of oxyhæmoglobin from hæmatin and a proteïd, 1017.
Bertoni, G., metanitrophenylsantoninmethane, 622.
Bertoni, G., and M. Zenoni, metanitro- and paranitro-diparadihydroxytriphenylmethane, 620.
Bertram, A., phenylthiocarbamide and imidothiocarbamates, 465.
Bertram, J., and H. Walbaum, oil of lavender and of bergamot, 1235.
Bertrand, G., colour reactions of carbohydrates, 664.
—— constitution of xylitol and xylose, 29.
—— xylose, 28.
Besana, C., estimation of free acids in butter, 924.
Besemfelder, E. See Baeyer.
Besson, A., boron phosphides, 273.
—— carbon chlorobromides, 771.
—— combination of ammonia with boron bromide and iodide, 771.
—— phosphorus bromonitride, 1272.
—— phosphorus chloronitride and phosphamide, 1152.
—— silicon thiochloride, 404.
Bettendorff, A., earths of the cerium and yttrium groups, 1400.
Bevan, E. J. See Cross.
Beyerinck, M. W., accumulation of atmospheric nitrogen in cultivations of *Bacillus radicicola*, 1019.
—— action at a distance of aqueous solutions on water vapour, 936.
Beysen, C. See Claus.
Bickes, T. See Jannasch.
Biedermann, J., derivatives of phenyl-α-hydroxycrotonic acid, 471.
—— new method of preparing the amide, anilide, and phenylhydrazide of mandelic acid, 473.
Biginelli, P., ethyl acetoacetate aldehydeuramides, 56.
Biginelli, P. See also Koerner.
Biltz, H., additive products of hydrogen iodide and nitriles, 1449.
—— lecture experiment on the diffusion of gases, 562.
Biltz, H. See also Brühl.
Bischler, A., formation of substituted indoles, 1465.
Bischoff, C. A., and A. Hausdörfer, derivatives of α-amidopropionic acid, 1336.
—— —— derivatives of naphthylglycocines, 1341.
—— —— derivatives of phenylglycocine and orthotolylglycocine, 1333.
—— —— paratolylglycocine and its derivatives, 1335.
Bischoff, C. A., and N. Mintz, anilidoisobutyric acids, 1338.
—— —— derivatives of α-amidobutyric acid, 1338.
—— —— derivatives of α- and β-naphthylidoisobutyric acids, &c., 1342.
—— —— toluidoisobutyric acids, 1339.
Bistrzycki, A., and G. Cybulski, phthalamidones, 1248.
Bistrzycki, A., and F. Ulffers, diacetylorthodiamines, 1197.
Bittó, B. v., behaviour of aldehydes and ketones with aromatic nitro-compounds, 1263.
—— sodium nitroprusside as a reagent for aldehydes and ketones, 924.
Bizzarri, D., carbazacridines: dehydration of amides in contact with diphenyl derivatives, 617.
—— methylcarbazacridine, 343.
Blachstein, gases of peptone blood, 363.
Bladin, J. A., action of ethyl acetoacetate on dicyanophenylhydrazine, 597.
—— condensation products of dicyanophenylhydrazine with aliphatic aldehydes, 596.
—— tetrazole, 1009.
—— triazole, 735.
—— triazole-derivatives, 637.
Blair, A. A., estimation of carbon in steel, 237.
Blau, F., αβ-dipiperidyl, 1365.
—— estimation of nitrogen in organic substances, 1515.
Bleicher, microscopic structure of the oölitic iron ore of Lorraine, 791.
Blomstrand, C. W., gadolinite, 1410.
Blümcke, A., change of the empirical and theoretical isotherms of mixtures of two substances with the temperature, 259.
—— labile conditions of equilibrium in mixtures of two substances at a temperature below the melting point of either, 936.
Blum, F., thymolglycuronic acid, 1116.
Blum, L., absorption apparatus for use in the estimation of sulphur in iron, 1376.

Blum, L., presence of lead in glass wool, 1375.
—— volumetric estimation of zinc, 534.
Blunt, T. P., indirect estimation of alcohol, 543.
Boas, J., estimation of hydrochloric acid in gastric juice, 97.
Boccard. See Di Boccard.
Bock, J. See Bohr.
Bode, J., derivatives of neurine and choline, 806.
Bodewig, A. See Schall.
Bodländer, G., behaviour of molecular compounds on dissolution, 1154.
—— formation of melilite during the burning of Portland cement, 416.
Böcher, P. See Claus.
Bölsing, F., and J. Tafel, acid hydrazides, 981.
Böttiger, E., quinolinehydrazines, 212.
Böttinger, C., condensation of anilpyruvic acid, 54.
—— derivatives of tannin, 181.
—— dimethylracemic acid, 698.
—— peptone salts of glutin, 1016.
Bogdanowska, V., dibenzyl ketone and dibenzylcarbinol, 851.
Bohr, C., combination of hæmoglobin with oxygen, 1369.
Bohr, C., and J. Bock, solubility of gases in water, 107.
Bohr, C., and S. Torup, oxygen in oxyhæmoglobin crystals, 1017.
Boisbaudran, L. de, samarium, 780.
—— spectra of gallium, 930.
—— supersaturation, 398.
Bois Reymond. See Du Bois Reymond.
Bokorny, T., nutrition of green plant-cells with formaldehyde, 1259.
Bone, A. W. See Lean.
Boniscontro, L. See Fileti.
Bornträger, A., decolorisation of wines, 543.
—— use of potassium hydrogen tartrate in titrating standard acids and alkalis, 525.
Bosio, G., influence of temperature on Griess' reaction for nitrites in water, 657.
Bouchardat, G., and J. Lafont, action of benzoic acid on turpentine, 199.
Bougarel. See Adrian.
Bourgeois, E. See Krafft, Spring.
Bourgeois, L., volatility of carbamide and its crystallisation by sublimation in a vacuum, 1309.
Bouriez, A., volumetric estimation of sulphates, 1377.
Bourquelot, E., detection and extraction of trehalose, 545.
Bourquelot, E., distribution of sugar in *Boletus edulis* and *B. aurantiacus*, 519.
—— starch in *Boletus pachypus*, 230.
Bouty, E., coexistence of dielectric power and electrolytic conductivity, 759.
Boyer, E., new method for the estimation of nitrogen, 237.
Brackett, R. N., and J. F. Williams, newtonite and rectorite, two new minerals of the kaolin group, 22.
Bradbury, R. H. See Smith.
Bradley, W. P., and F. B. Dains, action of acetic chloride on orthohydroxyaldehydes, 1458.
Braun, F., electrocapillary reactions, 394.
—— electrostenolysis, 393.
Braun, L., and R. Ebert, naphthalene dihydrosulphide and dithiocyanate, 1471.
Brauns, R., products of the weathering of diabase, 1412.
Bréal, E., aërobic nitrate-reducing ferment in straw, 1259.
—— fixation of free nitrogen during vegetation, 1508.
Brenzinger, K., cystin and cysteïn, 1111.
Bridge, J. L., quinoneoxime alkyl oxides, 1456.
Briggs, J. F. See Armstrong.
Brigham, C. P., double halogen salts of bismuth, 788.
Brochet, A., action of chlorine on isobutyl alcohol, 1292.
—— pyrogenic hydrocarbons in compressed gas, 797.
Brown, A. Crum, and J. Gibson, a rule for determining whether a given benzene derivative shall be a meta-di-derivative or a mixture of ortho- and para-di-derivatives, Trans., 367.
Brown, A. J., influence of oxygen and of concentration on alcoholic fermentation, Trans., 369.
Brown, D. R., and W. H. Perkin, jun., cryptopine, Proc., **1891**, 166.
Brown, H. T., on the search for a cellulose-dissolving (cytohydrolytic) enzyme in the digestive tract of certain animals, Trans., 352.
Brown, L. P., pea-nut, 1122.
Browning, P. E., separation of barium from calcium, 915.
—— separation of strontium and calcium nitrates by means of amyl alcohol, 915.
Bruck, P., diiodoacetylenedicarboxylic acid and diiodoacrylic acid, 431.

Brückner, C. See Conrad.
Brügelmann, G., characteristics of the alkaline earths, 17.
Brühl, J. W., action of sodium and carbonic anhydride on antipyrine, 1106.
—— alcohol of antipyrine, 730.
—— camphene and camphoric acid, 1240.
—— dipropargyl and benzene, 1436.
—— ethyl acetoacetate, 583.
—— terpenes and their derivatives, 200, 347, 624, 1100.
—— trimethylene, 1163.
Brühl, J. W., H. Biltz, A. Cantzler, and L. Reuter, terpenes and their derivatives, 623.
Brühl, J. W., and F. Müller, terpenes, 722.
Bruhns, G., and A. Kossel, adenine and hypoxanthine, 220.
Brun, E., compounds of cuprous iodide and ammonium thiosulphate, 1157.
Brunek, O., derivatives of paradiauilidobenzene, 1450.
Brunelle. See Combemale.
Bruyn. See Lobry de Bruyn.
Buehner, E., fermentation, 820.
Buchner, E., and H. Dessauer, phenyltrimethyleneearboxylic acids, 849.
Buehner, E., and A. Papendieck, bromacetamide, 827.
Buehner, E., and H. Witter, citric acid, 824.
—— —— symmetrical ethanetetracarboxylic acid, 824.
Buchner, G., analysis of white wax, 665.
—— cadmium sulphides, 778.
Buisine, A., and P. Buisine, adulteration of beeswax, 251.
—— —— utilisation of burnt pyrites in the manufacture of iron salts, 1281.
Buitchiehin, A. See Zelinsky.
Bunge, G., iron in the fœtal organism, 1502.
—— iron in the liver, 1503.
—— the in-take of iron by the fœtus, 516.
Burmeister, R. See Michaelis.
Burney, W. B., estimation of phosphoric acid, 1125.
Burns, P. S., dimolecular nitriles, 450.
Busch, A., and W. Koenigs, synthesis of β-chloroquinaldine, 505.
Busch, M., new synthesis of ketoquinazolines and thioquinazolines, 1495.
—— synthesis of phenotriazines, 734.
Busch, M., and M. Klett, cinnoline derivatives, 1494.

C.

Cain, J. C. See Bailey.
Cammerer, action of ferric chloride on metallic sulphides, 18, 278.
Cammerer, J. B., action of hydrogen peroxide on the oxides of molybdenum, tungsten, and vanadium, 944.
Campani, R. See Sestini.
Campbell, A. C., separation of iron from cobalt, nickel, and manganese, 103.
Camps, R., trimethylenedisulphone sulphide, 592.
—— trimethylenetrisulphone, 591.
Cantzler, A. See Brühl, Gattermann.
Canzoneri, F., hot mineral spring at Finca Huraeatao Selta, Argentine, 574.
Canzoneri, F. See also Arata.
Carbonelli, C. E., specific heat of the diamond, 761.
Carl, R. W. See Koenigs.
Carles, P., phosphoric acid in urine, 1115.
Carlson, M., acids from the dicyanhydrin of benzoylacetone, 1471.
Carnegie, D., sulphur tetroxide, 111.
Carnot, A., assay of antimony minerals, 918.
—— estimation of fluorine, 911.
—— fluorine in natural phosphates, 1055.
—— fluorine in recent and fossil bones, 1161.
—— proportion of fluorine in fossil bones of various ages, 1413.
Caro, N., hydroxyaurin and hydroxyaurinearboxylic acids, 855, 1469.
Carrara, G., condurangin, 1352.
—— new method of preparing dimethylethylsulphine and methyl ethyl sulphide, 1422.
—— thiourea, 1309.
Carrara, G. See also Spica.
Carriek, J. T., condensation of ethyl cyanaeetate and benzaldehyde; ethyl, α-cyanoeinnamate, 1086.
Catheart, W. R., and V. Meyer formation of closed-chain compounds by the elimination of bromine from the benzene nucleus, 992.
Cattaneo, C., thermal expansion of liquid bismuth, 259.
Cauffmann, M. See Orndorff.
Cauley. See MacCauley.
Causse, H., acetoneresorcinol, 1312.
—— dissolution of bismuth chloride in a saturated solution of sodium chloride; basic bismuth salicylate, 122.
—— orthophenylene hydrogen antimonite, 1078.

Causse, H., solubility of tricalcium phosphate and dicalcium phosphate in solutions of phosphoric acid, 684.
—— solution of antimonious chloride in saturated solutions of sodium chloride, 413.
Cavazzi, A., and D. Tivoli, action of hydrogen phosphide on an ethereal solution of bismuth tribromide, 279.
Cay. See McCay.
Cazeneuve, P., a violet from codeïne, 360.
—— conversion of gallic acid into pyrogallol, 1314.
—— ethylnitroketone and acetylnitroketone from camphosulphophenols, 1085.
—— formation of acetylene from bromoform, 421.
—— instability of carboxyl in phenolic acids, 1332.
—— nitroketone from camphosulphophenols, 999.
Cazeneuve, P., and Nicolle, rapid estimation of sulphuric acid, 659.
Chabrié, C., new proteïd from human blood serum, 224.
—— organic halogen and boron derivatives, 1316.
—— passage of substances in solution through mineral filters and capillary tubes, 1267.
Chalanay, L., and E. Knoevenagel, dicyanostilbene, 618.
—— —— stereoisomeric diphenylsuccinonitriles, 619.
Chalmot. See De Chalmot.
Chancel, F., propylamines and their derivatives, 804.
—— propylcarbamide and unsymmetrical dipropylcarbamide, 1421.
Chancel, F. See also Duvillier.
Chaplin, E. M., hydrazones of camphoric acid, 1481.
Chardonnet. See De Chardonnet.
Charpy, G., chemical equilibrium in solutions, 1146.
—— specific gravities of aqueous solutions, 765.
—— vapour pressure of aqueous solutions of cobalt chloride, 263.
Charpy, G. See also Gautier.
Charrin, A., toxicity of serum, 228.
Chassevant, A., double chlorides of lithium and metals of the magnesium series, 1275.
—— lithium copper chloride, 118.
Chassy, A., laws of electrolysis, 1037.
Chatard, T. M., analyses of pyroxene, 1409.
Chatelier. See Le Chatelier.
Chatin, A., truffles, 654.
Chattaway, W. See Allen.
Chittenden, R. H., E. P. Joslin, and F. S. Meara, ferments in pineapple juice, 650.
Chittenden, R. H., and T. B. Osborne, proteïds of the maize kernel, 379, 746, 749.
Chiussi, A. See Angeli.
Chorley, J. C., analysis of a slag from the manufacture of phosphorus in electrical furnaces, 1401.
Christ, A., composition of boiler incrustation, 17.
Christ, C. See Fittig.
Christensen, A., estimation of free alkaloïds and their molecular weight, 666.
Christensen, O. T., compounds of hydrogen diaminechromium thiocyanate with nitrogenous bases, 1000.
—— derivatives of chromium ammonium thiocyanate, 798.
Chuard, E., nitrification in organic media of acid reaction, 906.
Ciamician, G., constitution of naphthalene, 69.
Ciamician, G., and A. Angeli, constitution of tetrole-nuclei, 302.
Ciamician, G., and P. Silber, constituents of Paracoto bark, 62, 873.
—— —— pseudopelletierine, 1110.
—— —— the oxymethylene group in isosafrole, 972.
Ciamician, G., and C. U. Zanetti, molecular weight of the peptones, 1501.
Claisen, L., action of ethyl chlorocarbonate on ethyl sodacetoacetate, 1070.
—— constitution of ethyl acetoacetate and of the so-called formyl derivatives of ethereal salts and ketones, 1072.
—— isoxazoles, 506.
—— mixed azo-compounds, 710.
Clapp, G. H. See Hunt.
Clapp, R. R. See Comstock.
Clark, H. W. See Hazen.
Clark, J., direct estimation of arsenic in minerals and metals, 530.
—— separation of arsenic, antimony, and tin, Trans., 424.
Clarke, F. W., fractional analysis of silicates, 945.
—— petalite, spessartine, and willemite, 1411.
—— Tschermak's theory of the chlorite group and its alternative, 794.
Clarke, F. W., and E. A. Schneider, constitution of certain micas, vermiculites, and chlorites, 125.

Clarke, F. W. See also Schneider.
Classen, K., pure bismuth, 20.
Claus, A., alkyl and alkylene derivatives of cinchonic acid, and alkylene derivatives of cinchoxinic acid, 1488.
—— alkyl derivatives of cinchona alkaloïds, 1012.
—— aromatic alkyl ketones and their oximes, 985.
—— aromatic alkyl ketoximes, 1200.
—— γ-bromoquinoline, 875.
—— cinchona alkaloïds, 1249.
—— decomposition of glutaric acid at a high temperature, 40.
—— oximes, 1080.
—— oximes and the so-called stereochemistry, 50, 598.
—— quaternary ammonium bases of the quinoline series, 1358.
Claus, A., and L. Beck, nitration and bromination of parabromorthotoluic acid, 1207.
Claus, A., and C. Beysen, dinitroparatoluic acids and their derivatives, 177.
Claus, A., and P. Böcher, nitration of metachloroparatoluic acid, 173.
Claus, A., and N. Davidsen, nitration of orthochloroparatoluic acid, 172.
Claus, A., and J. Herbabny, nitration of and bromination of orthobromoparatoluic acid, 174.
Claus, A., A. Howitz, C. Massan, and G. Raps, halogen alkyl compounds of hydroxyquinolines, 876.
Claus, A., and H. Howitz, action of bromine on para- and ortho-hydroxyquinoline, 353.
Claus, A., and J. Joachim, nitration of orthonitroparatoluic acid, 176.
Claus, A., and A. Reh, bromination of bromobenzoic acids, 171.
Claus, A., and R. Seibert, dibromoparatoluic acid, 176.
Claus, A., and A. Stavenhagen, dichlorobenzoic acids, 1206.
Claus, A., and A. Weil, dibromobenzoic acids, 1205.
Claus, R. See Fittig.
Cleve, T. P., amidonaphthalenesulphonic acid, 345.
—— chloronaphthalenesulphonic acids, 1477.
—— 1 : 3 : 4-dichloronaphthalenesulphonic acid, 344.
—— 1 : 2-dicyanonaphthalene and 1 : 2-naphthalenedicarboxylic acid, 1477.
—— 1 : 2 : 2′-α-nitrochloronaphthalenesulphonic acid, 1478.
Clutterbuck, M. C. See Fittig.
Cohn. See Lassar Cohn.
Cohn, G., benzaldiphenylmaleïde and its derivatives, 482.
Cohn, G. See also Gabriel.
Cohn, R., occurrence of acetyl derivatives in the urine of animals after ingestion of aldehydes, 1504.
Colasanti, G., xanthocreatinine in the urine, 364.
Colby, G. E., and H. L. Dyer, analyses of Californian oranges and lemons, 1511.
Colefax, A., action of iodine on a mixture of sulphite and thiosulphate, Trans., 1083.
—— action of sulphurous acid on flowers of sulphur, Trans., 199.
—— investigation of the change proceeding in an acidified solution of sodium thiosulphate, where the products of the change are retained in the system, Trans., 176.
Coleman, J. B., rapid method of solution in the cold, 397.
Collan, U., autocatalysis, 1270.
Colli. See De Colli.
Collie, J. N., constitution of turpentine and camphor, 864.
Collie, N., and W. S. Myers, production of pyridine derivatives from the lactone of triacetic acid, Trans., 721.
Collot, A., rapid weighing on precision balances, 270.
Colman, H. G., the preparation of glycollic acid, Proc., **1892**, 72.
Colot, E., temperature of saturated vapours of various liquids under the same pressure, 1143.
Colson, A., stereochemistry of diacetyltartaric acid, 669, 758.
Combemale and Brunelle, physiological action of trimethylamine, 366.
Comstock, W. J., and R. R. Clapp, derivatives of aromatic formyl compounds, 707.
Comstock, W. J., and W. Koenigs, halogen derivatives of the cinchona alkaloïds, 1010.
Comstock, W. J., and H. L. Wheeler, alkyl derivatives of isosuccinimide, 701.
—— —— anilides, isoanilides, and their analogues, 705.
Coninck. See De Coninck.
Conrad, M., isarabic acid, 1432.
Conrad, M., and C. Brückner, halogen derivatives of malonic acid, 39.
Conrad, M., and L. Limpach, synthesis of quinoline derivatives by means of alkyl acetoacetates, 78.
Cooper, W. J. See Wanklyn.
Coquillion and Henrivaux, decomposition of hydrocarbons with steam, 288.

Cornevin, C., action of pilocarpine on the excretion of milk, 365.
—— influence of vegetable poisons on the germination of seeds, 228.
Costa, T., refractive power of isocyanides and nitriles, 757.
Costa, T. See also Nasini.
Cousin, H., homocatechol and two nitrohomocatechols, 1443.
Crafts, J. M., separation of the xylenes, 1134.
Craig, G., estimation of sulphur, 382.
Cramer, C., oximidoacetic acid, 699.
Crepieux, P., aromatic hydroxyketones, 62.
Cripps, R. A., estimation of volatile oil in copaiba, 244.
Crismer, L., crystalline products from lemon and bergamot oils, 349.
—— detection of tartaric acid in citric acid, 546.
—— detection of turpentine and other impurities in essences, 386.
—— formation of hydroxamic acids of the fatty acids by means of acid anhydrides, 828.
—— preparation of crystallised hydroxylamine, 771.
—— preparation of pure hydrogen peroxide solutions, 270.
—— reaction of certain essences with manganous salts, 386.
—— test for hydrogen peroxide, 381.
Cristaldi. See Grassi-Cristaldi.
Crocco, P., detection of albumin in urine, 667.
Cross, C. F., and E. J. Bevan, cellulose, 693.
—— —— constitution of the lignocelluloses, 129.
—— —— volumetric estimation of alumina, 535.
Crossley, A. W., optical properties of dulcitol and its derivatives, 1419.
Cuénot, L., respiratory value of hæmocyanin, 1370.
Cumenge, E. See Mallard.
Curchod. See Juillard.
Curtiss, R. S. See Fischer.
Curtius, T., azoimide, 112.
Curtius, T., and H. Lang, substitution of the azo-group for ketonic oxygen, 451.
Curtius, T., and L. Pflug, secondary asymmetrical hydrazines, 456.
Cybulski, G. See Bistrzycki.

D.

Daccomo, G., dithiocarbonic acids, 306.
Daccomo, G., metachlorothiophenol, 306.
—— ortho- and para-chlorothiophenol, 307.
Dains, F. B. See Bradley.
Dambergis, A. K., mineral springs of Edepsos, 418.
Damerow, F. See Liebermann.
Dancy, F. B., estimation of phosphoric acid in fertilisers, 1029.
Danner, E. W. See Gooch.
D'Arsonval, A., reactions of carbonic anhydride at high pressures, 274.
Dastre, A., formation of sugar in the organism when oxygen is deficient, 362.
Daubrée, native iron from Cañon Diablo, 947.
Davidsen, N. See Claus.
Davies, H. E., calcium phosphate from solution in acetic acid, 407.
Davies, H. O. See Herringham.
Davies, S. H., alkyl and acidyl sulphides, 300, 581.
Davies, S. H. See also Feith.
Davison, J. M., kamacite, tænite, and plessite from the Welland meteoric iron, 24.
De Boisbaudran. See Boisbaudran.
De Bruyn. See Lobry de Bruyn.
De Chalmot, G. See Günther.
De Chalmot, G. J. L., condensation products of furfuraldehyde with aromatic bases, 1451, 1452.
De Chardonnet, specific gravity of fibres, 1036.
Decker, H., action of alkalis on alkyliodides of the quinoline and acridine series, 879.
—— so-called γ-bromoquinoline, 630.
—— some ammonium compounds, 729.
De Colli, N., detection of alum in wines, 1523.
De Coninck, O., reactions of amidobenzoic acids, 847, 1380.
De Forcrand, constitution of pyrogallol, 1446.
—— dimetallic derivatives of dihydric phenols, 1185.
—— disodium glycol, 421.
—— monosodium catechol, 1184.
—— monosodium mannitol, 800.
—— monosodium resorcinol and monosodium quinol, 1184.
—— sodiotrimethylcarbinol: value of the tertiary alcoholic function, 1066.
—— sodium isopropoxide, 691.
—— sodium pyrogallol, 1313.
—— thermal function of phenol, 1042.
—— thermal value of the hydroxyl groups in glycol, 576.

De Forcrand, thermochemistry of sodium isopropoxide, 674.
—— value of the primary alcoholic function, 799.
Dehérain, P. P., phosphoric acid of the soil, 233.
De Koninck, L. L., estimation of free oxygen by means of nitric oxide, 97.
De Koninck, L. L., and M. Ledent, action of alkali sulphides on metals of the iron group, 537.
De Koninck, L. L., and E. Nihoul, estimation of soluble chlorides, bromides, and iodides, 527.
Delachanal. See Vincent.
Delacre, M., synthesis of symmetrical triphenylbenzene, 993.
De la Harpe, C. See Reverdin.
Delebecque, A. See Duparc.
Delépine, alcoholic solutions of ammonia, 1049.
Delisle, A., conversion of unsaturated acids into their stereochemical isomerides by soda, 297.
—— thetincarboxylic acids, 1433.
Del Lungo, C., pressure and specific volume of saturated vapours, 263.
Delmont, L., action of alkali sulphides on chloroform, 421.
Démètre-Vladesco, action of chlorine on some fatty ketones, 424, 810.
Demme, W., new albumin from protoplasm, 86.
De Mondesir, P., inorganic acid substance in soils, 1513.
Demyanoff, N., pentamethylene glycol and its oxides, 1292.
Denigès, G., action of pyridine bases on sulphites, 1103.
—— microscopic detection of sulphurous anhydride, 237.
—— preparation of bromoform from acetone and sodium hypobromite, 126.
—— preservation of solutions of metaphenylenediamine and its employment as a reagent, 1124.
Dennstedt, M., Étard's glycoline and Stoehr's dimethyldiazine, 633.
De Raczkowski. See Trillat.
Desch, C. H. See Meldola.
Desgrez, A. See Béhal.
Dessauer, H. See Buchner.
De St. Martin, L., estimation of carbonic oxide, 1128.
Desvignes. See Béhal.
Deutzmann, A., furfurylamine, 43.
De Varda, G., condensation of nitrobenzaldehydes with salicylic acid, 621.
—— nitro-derivative of methyl α-hydroxypropionate, 583.
Deventer. See Van Deventer.
De Vries, H. J. F., and A. F. Hollemann, phenylhydrazine acetate, 981.
Di Boccard, G., manganese hydroxide from the Euganeen, Italy, 689.
Dickhuth, F. See Liebermann.
Dieckmann, W., amidine picrates, 705.
Dieckmann, W. See also Bamberger.
Dieterici, C., theory of heat of dissolution and of osmotic pressure, 676, 765.
Dietze, A., new Chilian minerals: darapskite, lauarite, iodochromite, 124.
Ditte, A., iodic acid and its salts, 1388.
—— metallic borates, 565.
Dittrich, M., and V. Meyer, derivatives of ethyl dinitrophenylacetate, 178.
Divers, E., and T. Haga, imidosulphonates, Trans., 943.
Dixon, A. E., action of bromine on allylthiocarbimide, Trans., 545.
—— di-substituted semithiocarbazides, Trans., 1012.
—— chemistry of the compounds of thiourea and thiocarbimides with aldehyde-ammonias, Trans., 509.
—— isomerism amongst the substituted thioureas, Trans., 536.
Dobbie, J. J., and A. Lauder, corydaline, Trans., 244, 605.
Dollfus, W., configuration of aldoximes, 1174.
—— configuration of γ-ketoximic acids, 1202.
Domergue, A., and C. Nicolas, analysis of tea, 926.
Donath, E., analytical application of barium and hydrogen peroxides, 1031.
—— separation of manganese and zinc, 384.
Donner, A., benzeneazo-α-naphthylglycocine and its nitro-derivatives, 191, 1100.
Dormeyer, C. See Freund.
Dorp. See Van Dorp.
Doss, B., meteorite of Bisshof, Kurland, Russia, 1059.
Dott, D. B., assay of opium, 926.
Douglas, P., nitrogenous derivatives of thiophen and furfuran, 831.
Dralle, C. See Schall.
Drechsel, E., decomposition of albumin, 515.
—— new reaction of xanthine and allied compounds, 1534.
—— presence of cystin and xanthine in the horse's liver, 516.
Dreschsel, E., and T. R. Krüger, lysine, 1500.
Drechsel, E. See also Abel.
Drewes, D. See Otto.

Drouin, R. See Gautier.
Drown, T. M., and A. G. McKenna, direct estimation of aluminium in iron and steel, 102.
Dubelir, D., influence of water and sodium chloride on nitrogenous excretion, 904.
Duboin, A., artificial formation of potassium nepheline, 1286.
—— artificial production of leucite, 1161.
Du Bois Reymond, R., impure chloroform, 745.
Duclaux, supposed reaction of spermine, 1300.
Dudley, W. L., colours and absorption spectra of thin metallic films and of incandescent metallic vapours: electrical volatility, 1037.
Dufton, S. F., hydrazines of quinoline, Trans., 782.
Dumont. See Schmitz-Dumont.
Duncan, W., solubility of iodine in chloroform, 769.
Dunlap, F. L. See Freer.
Dunnington, F. P., distribution of titanic oxide on the earth's surface, 791.
Dunstan, W. R., mercuric zinc cyanide, a study of the mode of formation and properties of an insoluble double salt, Trans., 666.
Dunstan, W. R., and T. S. Dymond, the existence of two crystalline acetaldoximes, Trans., 470, Proc., 1892, 135.
Dunstan, W. R., and F. W. Passmore, the aconite alkaloïds. Part III. The formation and properties of aconine, and its conversion into aconitine, Trans., 395.
Dunstan, W. R., and J. C. Umney, the aconite alkaloïds. Part II. The alkaloïds of true *Aconitum napellus*, Trans., 385.
Duparc, L., and A. Delebecque, waters and basins of the Lakes of Aiguebelette, Paladru, Nantua, and Sylans, 1061.
Dussaud, F., refraction and dispersion of sodium chlorate, 1.
Duvillier, E., diethylamidocaproic acid, 294.
—— dimethylamidopropionic acid, 1302.
Duvillier, E., and F. Chancel, action of ammonia on bromisobutyric acid, 1302.
Dyer, H. L. See Colby.
Dymond, T. S., the existence of hyoscyamine in the lettuce, Trans., 90.
Dymond, T. S. See also Dunstan.

E.

Eakins, L. G., astrophyllite and Ischeffkinite, 22.
—— triplite and kaolin from the United States, 1406.
Easterfield, T. H., and W. J. Sell, anhydro-derivatives of citric and aconitic acids, Trans., 1003.
Ebert, R. See Braun.
Ebstein, W., physiological action of pentoses, 1506.
Eckart, C. U., German and Turkish rose oils, 203, 625.
Edeleanu, L., action of phenylhydrazine on carbamide, 1323.
Edeleanu. See also Istrati.
Edkins, J. S., absorption of water from the alimentary canal, 1258.
Edwards, V., estimation of nitrogen, 1125.
—— estimation of phosphoric acid in slags, 382.
Effront, J., conditions influencing the action of fluorides on fermentation, 906.
—— new method of yeast purification, 905.
Ehrenberg, A., and C. Purfürst, aconitine, 1254.
Ehrlich, S. See Pictet.
Eichengrün, A. See Graebe.
Eijkman, C., tropical anæmia, 363.
Eiloart, A., stereochemical models of organic molecules, 679.
Einhorn, A., preparation of α- and β-pyridyllactic acid from α-picoline, 75.
Einhorn, A., and L. Fischer, action of hypochlorous acid on tropine, 1014.
—— —— nitroatropine, 1014.
Einhorn, A., and B. Rassow, dihydroxyanhydroecgonine, 1015.
Eitner, P., action of sulphuric anhydride on nitriles, 713.
Eitner, P., and F. Krafft, mechanism of the formation of tricyanides from nitriles and acid chlorides in presence of aluminium chloride, 1183.
Elbs, K., paranthracene, 347.
Elfeldt, P., oxyazolines and pentoxyazolines, 213.
Elfeldt, P. See also Gabriel.
Eliasberg, J., and P. Friedländer, condensation of orthamidobenzaldehyde, 1106.
Elion, H., estimation of maltose, dextrose, and dextrin in beer wort, 248.
Elkeles, G., cineolic acid, 1480.
Ellenberger and Hofmeister, digestion of starch by dogs, 516.
Emich, F., action of potassium hydroxide on nitric oxide, 940.

Emich, F., behaviour of nitric oxide at high temperatures, 940.
—— preparation of nitric oxide, 939.
—— reaction between nitric oxide and oxygen, 940.
Emmerling, A., earth-nut meal, 92.
Emmerton, F. A., estimation of phosphorus in pig-iron, steel, and iron ores, 529.
Engel, the variations in colour of cobalt chloride, 569.
Engel, R., influence of ammonia on the solubility of ammonium chloride, 276.
—— reaction between potassium permanganate and hydrogen peroxide, 277.
Ephraim, J., amidoquinolines, 1488.
Eppens, A. See Koenigs.
Erdélyi, J., detection of foreign fats in butter, 1532.
Erdmann, H., condensation of levulinic acid with aldehydes, 147.
Erlenbach, A., action of sodium on ethyl chloracetate, 953.
—— preparation of symmetrical dichloracetone, 952.
Ernst, C., putrefaction of bile, 518.
Errera, G., action of potassium hypobromite on the amide of campholic acid, 1345.
Errera, G., and G. Baldracco, paramethylhydratropic acid, 605.
Essner, J. C., composition of some natural subterranean waters near Port-Vendres. 285.
—— precipitation of copper by iron, and the action of iron on ferric solutions, 276.
—— siphon for hot liquids, &c., 270.
Étard, A., colorations of solutions of cobalt, and the state of the salts in the solutions, 278.
—— compounds that accompany chlorophyll in leaves, 746.
—— formation of bromaldehydes and bromoketones by the action of bromine on alcohols of the ethyl series, 809.
—— method of analysis of chlorophyllic extracts: nature of chlorophyllane, 1136.
—— organic liquids as solvents for metallic salts, 558.
—— state of salts in solution: sodium sulphate and strontium chloride, 397.
—— the chlorophyllic substances of the pericarp of the grape, 874.
Etz, P. See Jannasch.
Evans, W. P., attempts to prepare metallic chromium from chromic fluoride, 19.
Evers, F., new condenser for laboratory purposes, 400.
Evershed, F. See Green.
Ewan, T., and W. R. Ormandy, a method of measuring the vapour pressures of solutions, Trans., 769.

F.

Fabris, L., detection of atropine, 1534.
Failyer, G. H. See Willard.
Falières. See Barthe.
Farnsteiner, K., volumetric estimation of combined sulphuric acid, 1515.
Farrington, O. C., chemical composition of iolite, 793.
Fauconnier, A., action of phosphoric chloride on ethyl oxalate, 588.
Feist, F., chlorinated diacetylacetone, 811.
—— constitution of dehydracetic acid, 587.
—— dehydracetic acid, 584.
—— dehydracetic chloride, 587.
Feit, W., ascharite, a new borate, 792.
—— heintzite, 791.
Feit, W., and K. Kubierschky, extraction of rubidium and cæsium compounds from carnallite, 1395.
—— —— use of bromic acid in quantitative analysis, 910.
Feith, E., derivatives of mesitylene, 329.
—— methyl mesitylenecarboxylate, 715.
Feith, E., and S. H. Davies, action of hydroxylamine on acetomesitylene, 314.
Fermi, C., solubility of fibrin, 897.
Ferratini, A. See Zatti.
Field, Miss E., chromic acid, Trans., 405.
Fileti, M., analysis of the barium group, 660.
Fileti, M., and V. Abbona, hydroxyderivatives of cumonitrile, 595.
Fileti, M., and L. Boniscontro, oxidation products of paradibromohomocumic acid, 604.
Filsinger, F., analysis of crude glycerol, 544.
Fink, E., phosphopalladious compounds, 1285.
Fiquet, E., synthesis of unsaturated nitriles, 1340.
Firtsch, G., rumpfite, 417.

Fischer, E., new isomeride of galactonic acid and of mucic acid, 299.
Fischer, E., and R. S. Curtiss, optically isomeric gulonic acids, 822.
Fischer, E., and J. Hertz, reduction of mucic acid, 824.
Fischer, E., and K. Landsteiner, glycollaldehyde, 1424.
Fischer, E., and O. Piloty, new pentonic acid and the second inactive trihydroxyglutaric acid, 437.
Fischer, E., and A. J. Stewart, aromatic sugars, 1447.
Fischer, E., and others, sugars richer in carbon from glucose, 1164.
Fischer, L. See Einhorn.
Fischer, O., orthodiamines, 1472.
Fischer, O., and E. Hepp, formation of indulines, 1476.
—— —— studies in the induline group, 341.
Fischer, O., and H. Wreszinski, action of formaldehyde on orthodiamines, 1496.
Fischer, P., action of ammonia and aniline on negatively substituted halogenised benzenesulphonic acids, 331.
—— chloronitrobenzenesulphonic acids, 182.
Fischer, W. See Jacobson.
Fittig, R., decomposition of dibromides of unsaturated acids by warm water and dilute alkalis, 959.
—— lactonic acids, lactones, and unsaturated acids, 812, 956.
Fittig, R., and C. Christ, some new lactones, 962.
Fittig, R., and R. Claus, new derivatives of coumarin, 988.
Fittig, R., and M. C. Clutterbuck, tetrolic acid, 961.
Fittig, R., and J. Hillert, decomposition of dibromocaproic acid, 960.
—— —— oxidation of hydrosorbic acid, 959.
Fittig, R., and W. D. Hoeffken, divalolactone, 814.
Fittig, R., and E. Kochs, oxidation of crotonic acid and isocrotonic acid, 957.
Fittig, R., and E. Mayer, oxidation of hydrocinnamenylacrylic acid, 986.
Fittig, R., and P. Obermüller, oxidation of phenylisocrotonic acid, 986.
Fittig, R., P. Obermüller, and C. Schiffer, decomposition of phenyldibromobutyric acid, 987.
Fittig, R., and G. Parker, condensation of pyruvic acid with dicarboxylic acids, 814.
Fittig, R., and R. Ruer, oxidation of cinnamic acid, 986.
—— —— oxidation of ethylcrotonic acid, 958.
Fittig, R., and J. Stern, decomposition of phenyldibromovaleric acid, 987.
—— —— hydrocinnamenylacrylic acid, 988.
Fittig, R., and K. T. Ström, action of sodium ethoxide on butyrolactone, 813.
Fittig, R., and K. Urban, decomposition of dibromovaleric acid, 960.
—— —— oxidation of allylacetic acid, 958.
Flavitzky, F., correlation of oxygen and hydrogen compounds of the elements, 1270.
Fleischhauer, H., condensation of cyanides with ethereal salts. 431.
Fleissner, F. See Lippmann.
Fleurent, E., action of potassium cyanide on ammoniacal cupric chloride, 1065.
—— ammonio-copper ammonium cyanide, 420.
Fleury, G., estimation of tannin, 1135.
Flink, G., braunite and friedelite from Sweden, 1405.
Fock, A., and K. Klüss, ammonium dithionate hydrochloride, 13.
—— —— thiosulphates, 12.
Foerster, F., action of superheated water and solutions of alkalis and salts on glass, 1401.
—— derivatives of carbonyl chloroplatinites, 352.
Foerster, F. See also Mylius.
Foerster, O., estimation of phosphoric acid by the molybdic process, 1519.
Fogh, J., sugars, 933.
Foote, A. E., discovery of diamonds in meteoric iron, 284.
—— new meteoric iron from Maryland, 794.
Forbes, M., apparatus for washing precipitates, 1513.
Forcrand. See De Forcrand.
Formánek, E., formation of uric acid from cyanacetic acid and carbamide, 149.
—— influence of hot baths on the excretion of nitrogen and uric acid from the human system, 1503.
Forssel, G., action of ethylenediamine on thiamides, 1247.
Forte, O. See Oglialoro.
Foster, W., note on the carbon deposited from coal-gas flames, PROC., **1892**, 46.

Fraenkel, S. See Kerry.
Franceschi, G., volumetric estimation of arsenic acid, 1519.
—— volumetric estimation of gold, 1526.
Francesconi, L., santonic acid, 1352.
Franchimont, A. P. N., acetaldoxime, 951.
—— action of nitric acid on the amidines. 951.
Frank, B., assimilation of free nitrogen in plants in its dependence on species, on nutrition, and on soil, 370.
—— to what extent is atmospheric nitrogen assimilable?, 1507.
Franke, E., action of sulphonic chlorides on orthamidobenzamide, 334.
Frankel, L. K., oxidation of arsenic by the electric current, 752.
Frankland, Mrs. G. C., morphological characterisation of *Bacillus ethacetosuccinicus*, TRANS., 275.
Frankland, P. F., and W. Frew, a pure fermentation of mannitol and dulcitol, TRANS., 254.
Frankland, P. F., and J. S. Lumsden, decomposition of mannitol and dextrose by the *Bacillus ethaceticus*, TRANS., 432.
Frankland, P. F., and J. MacGregor, fermentation of arabinose with the *Bacillus ethaceticus*, TRANS., 737.
Franzek, C. J. See Jannasch.
Fredericq, L., hæmocyanin, 1370.
Freer, P. C., ethyl acetoacetate, 953.
—— lecture experiment illustrating the effusion of gases, 1150
Freer, P. C., and F. L. Dunlap, hydrolysis of substituted ethyl acetates, 1148.
Freinkel. M. See Kehrmann.
French, W., estimation of gold, tin, and cadmium in alloys, 1030.
Fresenius, R., Julianen and Georgen springs at Eilsen, 796.
—— separation of barium from calcium, 100.
Fresenius, W., recognition of potato starch sugar in wines, 922.
Fresenius, W., and F. Ruppert, solubility of calcium and strontium chromates in dilute alcohol, and the separation of these metals as chromates, 914.
Freudenberg, H., a new principle of electrolytic separation of metals, 1521.
Freund, E., volumetric estimation of sulphuric acid in urine, 1377.
Freund, M., and C. Dormeyer, hydrastine, 223.
Freund, M., and W. Josephy, alkaloïds of the root of *Corydalis cava*, 1366.
Freund, M., and W. Rosenstein, cinchonine, 892.
Freund, M., and F. Schönfeld, interaction of nonylamine and nitrous acid, 132.
Freund, M., and H. Wolf, action of thiocarbonyl chloride on aromatic thiocarbamides, 983.
Freund, M., and others, biazolones, 508.
Frew, W. See Frankland.
Freyer, F., and V. Meyer, boiling point of zinc chloride and bromide, and ignition temperature of electrolytic gas, 680.
Fricke, E., estimation of nitrogen in nitrates, 527.
Friedel, C., ethyl camphorates and isocamphorates, 500.
Friedländer, P., and S. Szymanski, nitration of β-naphthylamine, 1232.
Friedländer, P. See also Eliasberg.
Friswell, R. J., note on the action of dilute nitric acid on coal, PROC., 1892, 9.
Fromm, E., phenyldithiobiuret, 844.
Fromm, E. See also Baumann.
Früstück, E. See Wallach.
Fubino, S., detection of vegetable fibre in silk or woollen tissue, 667.
Fuchs, F., a new combustion furnace, 1514.
Fuchs, O. See Zincke.

G.

Gabriel, S., ε-chloramylamine and synthesis of piperidine, 717.
—— δ-chlorobutylamine: synthesis of pyrrolidine, 131.
—— estimation of cellulose, 923.
—— preparation of primary amines by means of potassium phthalimide, 157.
—— thio-derivatives of ethylamine, 130.
Gabriel, S., and G. Cohn, diphenylmaleïc anhydride, 178.
Gabriel, S., and P. Elfeldt, mesophenylpentoxazoline, 212.
Gabriel, S., and R. Jansen, quinazolines, 217.
Gabriel, S., and A. Neumann, formation of oxazolines, 1331.
Gabriel, S. See also Hofmann.
Gaess, F., nitro-β-naphthols, 1229, 1341.

Gal, J., formation of plastic sulphur from sulphur vapour, 1150.
Ganelin, S., and S. v. Kostanecki, constitution of orthohydroxyazo-dyes, 506.
Gans, L. See Benedikt.
Garelli, F., derivatives of cyanacetophenone, 845.
—— oximes of some ketonic acids, 327.
Garny, F., action of hydroxylamine on derivatives of succinic and glutaric acids, 136.
Garrod, A. E., hæmatoporphyrinuria, 1506.
—— urohæmatoporphyrin, 744.
Garzarolli-Thurnlackh, K., γ-trichloro-β-hydroxybutyric acid: new synthesis of malic acid, 429.
Garzino, L., tetrahydropyrazine, 633.
Gassend, A., detection of sesame oil in olive oil, 1133.
—— presence of boric acid in products of the soil, 93.
Gattermann, L., and A. Cantzler, aromatic isocyanates, 832.
Gattermann, L., and R. Hölzle, replacement of the hydrazine group by halogens, 842.
Gattermann, L., E. S. Johnson, and R. Hölzle, acid hydrazides, 843.
Gattermann, L., and O. Neuberg, synthesis of dehydrothiotoluidine, 839.
Gautier, A., origin of the colouring matters of the vine: ampelochroic acid, 1242.
Gautier, A., and R. Drouin, fixation of atmospheric nitrogen by arable soils, 522.
Gautier, A. See also Hanriot.
Gautier, H., and G. Charpy, direct combination of chlorine and bromine with metals, 118.
Gautier, H. See also Moissan.
Gawalovski, A., block support for tubes, 9.
Gaze, R., propionates, 140.
Geelmuyden, H. C., estimation of uric acid, 1032.
Genth, F. A., hübnerite, hessite, bismutite, and natrolite, 793.
Genvresse, P., synthesis of tartaric acid, 822.
Georgescu, M., tetrahydroketoquinoxalines, 886.
Georgescu. See also Istrati.
Georgievics, G. v., action of carbonic anhydride and ferric hydroxide on tricalcium phosphate, 408.
Gérard, vegetable cholesterol, 1294.
Gérard, E., derivatives of daturic acid, 582.
Gerlach, M., β-ethylthiophen and thiophen-αβ-dicarboxylic acid, 829.
Gernez, D., compounds of sorbitol and perseïtol with molybdates, and their rotatory power, 422, 800.
Geyger, A. See Töhl.
Gfeller, E. See Graebe.
Gibbins, B. H., estimation of iron and aluminium by the Glaser method, 755.
Gibbs, W., electrolytic estimation of metals as amalgams, 753.
Gibson, C., differences in the estimation of reverted phosphoric acid by the American official method, 1126.
Gibson, J. See Brown.
Giesel, F., alkaloïds from Javan coca leaves, 361.
Gigli, T., estimation of iodates in potassium iodide, 657.
Gilbault, H., compressibility of saline solutions, 766.
Gilbert, J. H. See Lawes.
Gill, A. C., minerals from the chrome iron ore deposits of Maryland, 1057.
Gill, A. H., improved pipette for gas absorptions 1124, 1374.
Gilpin, J. E., mercurous hypochlorosulphite, 780.
Giorgis, G., action of hydrogen peroxide and of water saturated with carbonic anhydride on magnesium, 17.
—— siliceous sand of Monte Soratte, 23.
Giorgis, G. See Piccini.
Girard, A. C. See Müntz.
Giustiniani, E., action of heat on the hydrogen malates of methylamine and benzylamine, 820.
Glaser, gasometric estimation of nitric acid, 1375.
Glaser, C., estimation of aluminium phosphate, 1523.
Glatzel, E., antimony thiophosphate, 413.
Glendinning, T. A. See Moritz.
Glenk, R., *Cicuta maculata*, 232.
Glogner, M., specific gravity of the blood of Europeans living in the tropics, 363.
Glücksmann, C., β-trimethylethylidenelactic acid, 38.
Göttig, C., dichlorhydrin parahydroxybenzoate, 715.
—— isomeric dichlorhydrin metahydroxybenzoate, 471.
Goldbeck, O., nitrogenous derivatives of parahomosalicylic acid, 318.

Goldberg, B, formation of rosaniline, 340.
Goldberg, G., P. Kunz, and K. Kraut, glycocine and its derivatives, 294.
Goldschmidt, H., and H. Bardach, diazoamido-compounds, 977.
Goldschmidt, H., and A. Pollak, hydroxyazo-compounds, 974.
Goldschmidt, H., and E. Zanoli, oximes of furfuraldehyde, thiophenaldehyde, and œnanthaldehyde, 1433.
Goldschmiedt, G., opianic acid, 179.
Goldschmiedt, G., and R. Jahoda, ellagic acid, 990.
—— —— substances contained in the petals of *Gentiana verna*, 205.
Gonnet. See Jablin-Gonnet.
Gooch, F. A., and E. W. Danner, separation of antimony from arsenic, 541.
Gooch, F. A., and H. W. Gruener, estimation of antimony, 242.
Gooch, F. A., and T. S. Hart, detection and estimation of potassium spectroscopically, 913.
Gooch, F. A., and C. G. Smith, estimation of chlorates, 236.
Gore, G., changes of E.M.F and temperature by mixing electrolytes, 930.
—— changes of voltaic energy of alloys during fusion, 254.
—— relation of E.M.F. to latent heat, sp. gr., &c., of electrolytes, 257.
Gorgeu, A., decomposition of silver permanganate, 942.
Gossart, E., application of capillary phenomena to the analysis of liquids, 236.
Gottlieb, E., estimation of fat in milk, 549.
Gouy, electrocapillary phenomena, 760.
—— electrocapillary phenomena and differences of contact potential, 553.
Gowan. See McGowan.
Goyder, G. See Rennie.
Graebe, C., and A. Eichengrün, action of heat on salicylic acid, 1208.
—— —— behaviour of aromatic hydroxyketones with sulphuric acid and with ammonia, 1226.
—— —— hydroxyketone dyes, 1224.
Graebe, C., and E. Gfeller, oxidation of acenaphthene, 863.
Graebe, C., and K. Lagodzinski, phenylanthranilic acid and acridone, 1086.
Graffenberger, L., decomposition of fibrin, gelatin, peptone, and asparagine in the human body, 904.
Graffenberger, L., estimation of free hydrochloric acid in the stomach, 236.
Gram, J., paradiamidodiphenylmethane, 618.
Grande, E., phenolphthaleïn ethyl ether, 1096.
Grandis, V., chrysophanic acid, 1354.
Grandmougin, E., and O. Michel, homonuclear amidonaphthols and related derivatives, 861.
Granger, copper phosphides, 410.
—— mercury phosphide, 1398.
Grassi-Cristaldi, G. See Gucci.
Grawitz, S., dyeing with aniline-black in the dry way, 323.
Gray, J., apparatus for determining the flashing point of heavy mineral oils, 542.
Green, A. G., and F. Evershed, estimation of nitrous acid, 751.
Gréhant, N., absorption of carbonic oxide by the blood of a living mammifer, 743.
—— detection of minute quantities of carbonic oxide, 99.
Griepenkerl, J. See Wallach.
Griesbach, A., coagulation of blood, 1112.
Griffiths, A. B., blood of invertebrata, 648.
—— chlorocruorin, 1256.
—— direct absorption of ammoniacal salts by plants, 229.
—— hæmocyanin, 898.
—— new leucomaïne, 1367.
—— pinnaglobin, a new globulin, 1016.
—— ptomaïnes of infectious diseases, 1258.
—— pupin, 1501.
Grimaldi, G. P., measurement of the sp. heat of liquids at temperatures above their boiling points under ordinary pressures, 761.
Grimaux, E., quinone methiodides, 1363.
Grimaux, E., and A. Arnaud, bases homologous with quinine, 1253.
—— —— conversion of cupreïne into quinine, 892.
Gripper, H., rapid method of determining the composition of lubricating oils, 665.
Grittner, A., detection of resin oil in fatty and mineral oils, 548.
Gröger, M., a new oxyiodide of lead, 1280.
Grohmann, A., action of ammonia and aniline on halogen-substituted nitrobenzoic acids, 326.
Grosjean, L., decylene and its derivatives, 691.

Groves, E. W., estimation of uric acid, 546.
Groves, E. W. See also Herringham.
Gruener, H. W. See Gooch.
Grünhut, L., Rose's process for the estimation of alcohol, 1031.
Grünwald, A., Hasselberg's so-called second or compound hydrogen spectrum and the structure of hydrogen, 1381.
Grützner, B., stability of potassium permanganate solution, 1524.
Guareschi, I., action of ethyl cyanacetate on organic bases, 1071.
—— platinum thiocyanates and platinothiocyanates, 286.
—— γ-substituted hydantoïns: carbamido-acids, 827.
Gucci, P., and G. Grassi-Cristaldi, derivatives of santonin, 869.
Guenez, E., arsenic cyanide, 1164.
Günther, A., G. de Chalmot, and B. Tollens, formation of furfuraldehyde from glycuronic acid derivatives and from albumin, 1433.
—— —— —— estimation of furfuraldehyde and of pentoses, 388.
Guillemin, G., micrographic analysis of alloys, 1399.
Gumlich, G., the excretion of nitrogen in urine, 1503.
Gunning, J. W., preparation of raffinose from molasses, 422.
Guntz, action of carbonic oxide on iron and manganese, 568.
Gustavson, G., action of zinc-dust and alcoholon chlor-α-dibromhydrin, 1293.
Guye, P. A., molecular dissymmetry, 399, 758.
—— stereochemistry and the laws of rotatory power, 759.

H.

Haack, K., separation of phosphoric and arsenic acids from mercury, and of nitric acid, chlorine, and sodium from mercury, phosphoric, and arsenic acids, 530.
Haegele, E., condensation products of amidophenols, 1451.
Haeussermann, C., and C. Beck, action of chlorine on orthonitrotoluene, 1437.
Haga, T. See Divers.
Haig, A., estimation of uric acid, 1133.
Haines, R., iodine number for lard oil by the Hübl method, 664.
Hairs, E. See Jorissen.
Haitinger, L., emission spectra of neodymium and præsodymium oxides and of luminous solids containing neodymium, 2.
Halberstadt, E. See Täuber.
Haldane, J., respiration apparatus, 1257.
Haldane, J., and J. L. Smith, air vitiated by respiration, 1502.
Hall, W. F., action of nascent hydrogen and nascent oxygen on nitric acid, 680.
Haller, A., action of sodium alkyloxides on camphor: preparation of alkylcamphors, 72.
—— alkylcyanocamphors and alkyl benzeneazocamphocarboxylates, 1344.
—— constitution of camphoric acid, 1347.
—— function of camphoric acid, 1346.
—— modes of formation of substituted imides, 1204.
Haller, A., and A. Held, ethyl bromacetoacetate and cyanacetoacetate, 818.
—— —— haloïd derivatives of ethyl acetoacetate, 697.
Halliburton, W. D., mucin in myxœdema, 1117.
Hamberg, A., minerals from the Harstigen mine, Sweden, 1411.
Hambly, F. J., detection of nickel and cobalt, 1525.
Hamilton, R., precipitation of phosphorus from solutions of iron and steel, 911.
Hammarsten, O., detection of hæmatoporphyrin in urine, 1136.
—— hæmatoporphyrin in urine, 649.
Hammerich, H., action of silver cyanide on dibenzylchlorocarbamide and paraditolylchlorocarbamide, 1084.
—— derivatives of dibenzylcarbamic, paraditolylcarbamic, and benzylparatolylcarbamic acids, 1083.
—— tetrabenzyloxamide and tetraparatolyloxamide, 1084.
Hampe, W., estimation of bismuth in silver slags, 919.
—— estimation of manganese by the chlorate method, 1132.
—— estimation of silicic acid in fluorides, 1127.
Handl, A., and R. Přibram, viscosity of liquids, 1143.
Handy, J. O. See Hunt.
Hanriot, action of hydroxylamine on ketonic nitriles, 79.
—— assimilation of carbohydrates, 742.
Hanriot and A. Gautier, assimilation of carbohydrates, 742.
Hanriot, M., and C. Richet, physiological action of nickel carbon oxide, 365.

Hantzsch, A., action of hydroxylamine on chloral, 699.
—— aliphatic stereoisomeric glyoximes, 693.
—— configuration of aliphatic ketoximes, 426.
—— configuration of the aldoximeacetic acids or β-oximidopropionic acids, 1069.
—— decomposition products of anilic acid, 834.
—— isomeric oximes and hydrazones, 1083.
—— nomenclature of stereoisomeric nitrogen compounds and of rings containing nitrogen, 312.
—— relations between constitution, configuration, and chemical behaviour of oximes, 1175.
—— so-called ethyl carbacetoacetate, 819.
Hantzsch, A., and F. Kraft, stereochemical isomerism of nitrogen compounds, 338.
Hantzsch, A., and A. Miolati, dissociation constants of stereoisomeric nitrogen compounds, 1268.
Hantzsch, A., and H. Schiffer, constitution of ethyl chloracetoacetate, 697.
Harker, J. A., reaction of hydrogen with chlorine and oxygen, 1147.
Harley, V., disappearance of sugar from the blood, 363.
Harnack, E., ash-free albumin, 645.
Harpe. See De la Harpe.
Harries, C. D., methyl orthohydroxycinnamyl ketone and its derivatives, 169.
—— reduction of salicylaldehyde, 168.
Harrington, B. J., so-called amber of Cedar Lake, Canada, 573.
Hart, T. S. See Gooch.
Hartley, W. N., action of heat on solutions of chromium salts, 571.
—— the acid action of drawing paper of different makes, Proc., 1892, 19.
Hartmann, A. See Liebermann.
Hartung, L., hexamethyleneamine, 1173.
Haubner, G., action of sulphurous anhydride on crotonaldehyde, 424.
Hausdörfer, A. See Bischoff.
Hausser, nitrosulphobenzoic acid, 479.
Hausser, J. See Muller.
Hawkins, E. M. See Meldola.
Hazen, A., estimation of the dissolved matter in water, 920.
—— new colour standard for natural waters, 1527.
Hazen, A., and H. W. Clark, estimation of nitrates in water, 243.
Heaton, C. W., and S. A. Vasey, analysis of peptones, 1535.
Hébert, A., development of cereals, 1119.
—— occurrence in plants of a gum giving rise to xylose by saccharification, 1371.
Hecht, O., thiobiurets, 703.
—— thiocarbamides, cyanocarbamides, and cyanothiocarbamides, 702.
Hector, D. S., action of oxidising agents on aliphatic thiocarbamides, 292.
Heermann, P., 1 : 4-amidonaphthol ethyl ether and its derivatives, 1097.
—— organic phosphorus compounds, 875.
Hehner, O., estimation of boric acid, 384.
Heiber, F., action of methylchloroform and phenylchloroform on alkaline solutions of phenols, 308.
—— diethyl hydrofurfuryllutidinedicarboxylate and its derivatives, 1362.
Heidenreich, A., and V. Meyer, formation of diphenylamine from orthobromobenzoic acid, 1188.
Heim, F., blue colouring matter in the blood of crustaceæ, 898.
Heim, F. See also Abelous.
Heisch, C., obituary notice of, Trans., 489.
Heise, P., and A. Töhl, action of aluminium chloride on aromatic hydrocarbons, 1309.
Held, A. See Haller.
Hell, C., and R. Poliakoff, action of α- and β-naphthylamine on ethyl bromosuccinate, 860.
—— —— amido- and anilido-derivatives of succinic acid, 819.
Helle, J., orthotolidinedisulphonic acid, 1466.
Hemmelmayr, F. v., base obtained from pyridine, 504.
Hempel, W., new desiccator, 524.
Henrich, F., absorption coefficients of gases, 1043.
Henrichsen, S., magnetism of organic compounds, 672.
Henrivaux. See Coquillon.
Henry, P., direct synthesis of primary alcohols, 27.
—— reciprocal transformation of lactones and hydroxy-acids, 1303.
Hepp, E. See Fischer.
Herbabny, J. See Claus.
Héricourt, J., and C. Richet, toxic action of blood and of various tissues, 228.
Hermens, R. See Michaelis.

Herringham, W. P., and H. O. Davies, excretion of uric acid, 365.
Herringham, W. P., and E. W. Groves, excretion of uric acid, urea, and ammonia, 365.
Herty, C. H., double halogen salts of lead, 779.
Hertz, J. See Fischer.
Herzberg, W., and M. Polonowsky, action of nitrous acid on tetramethyldiamidobenzophenone, 185.
Herzfeld, A., pectin substances, 291.
Herzig, J., euxanthic acid and euxanthone, 1354.
—— fluorescin, galleïn, and aurin, 1319.
Hesse, A. See Wallach.
Hesse, O., alkaloïds of belladonna, 1498.
—— *Aristolochia argentina*, 894.
—— behaviour of cupreïne and quinine with methyl iodide, 221.
—— cincholine and fluoroline, 1492.
—— conversion of cupreïne into quinine, 1010.
—— isocinchonine, 222.
—— quinine hydrochlorides, 514.
—— sulphonic acids of cinchona alkaloïds, 514.
Heupel, A. See Paal.
Heuser, A., and C. Stoehr, methyldipyridyls, 75.
Heusler, F., action of acetic anhydride on diazoamido-compounds, 458.
—— lignite tar, 1075.
Heycock, C. T., and F. H. Neville, isolation of a compound of gold and cadmium, Trans., 914.
—— —— on the lowering of the freezing points of cadmium, bismuth, and lead when alloyed with other metals, Trans., 888.
Heydecke, E. See Otto.
Heymann, B., synthesis of indigodisulphonic acid, 69.
Hill, T. E., the Werner-Schmid method of milk analysis, 390.
Hillebrand, W. F., new analysis of uraninite, 283.
—— samarskite from Colorado, 416.
Hillebrand, W. F., and W. H. Melville, isomorphous thorium and uranous sulphates, 571.
Hillert, J. See Fittig.
Hills, T. H., obituary notice of, Trans., 489.
Hiltner, L., approximate estimation of adulteration of earth-nut cake and meal, 1535.
Hinrichs, G., boiling point curves of the normal paraffins, 947.
—— boiling points of paraffin derivatives, 797.
—— calculation of boiling points of normal isomeric ethereal salts of the fatty series, 260.
Hinrichs, G., calculation of the specific heat of liquids, 2.
—— establishment of fundamental formulæ for the calculation of moment of inertia, 948.
—— mechanical determination of the boiling points of alcohols and acids, 1039.
—— mechanical determination of the boiling points of compounds with complex terminal substitution, 1039.
—— mechanical determination of the boiling points of compounds with simple terminal substitution, 948.
—— pressure of saturated water vapour, 396.
Hinsberg, O., action of amido-bases on sodium glyoxalsulphonate, 1458.
—— behaviour of certain ketonic acids towards hydrogen sodium sulphite, 148.
—— benzenesulphonamides and mixed secondary amines, 64.
—— benzenesulphonitramide, 850.
—— methylhydroxytoluquinoxaline and the constitution of the compounds obtained from α hydroxyanils and orthodiamines, 1359.
Hinsberg, O. See also Autenrieth.
Hinsdale, S. J., estimation of gallotannic acid, gallic acid, and tannin, 390.
Hirsch, R., new synthesis by means of diazo-compounds, 1198.
Hise. See Van Hise.
Hjelt, E., allylethylsuccinic acid and allylmethylsuccinic acid, 697.
—— orthohydroxymethylbenzoic acid, 715.
Hodgkinson, W. R., the action of sodium on ethereal salts. Part III. Benzyl orthotoluate, Proc., **1891**, 167.
Hodgkinson, W. R., and L. Limpach, some new bases. Part I, 6:1:4:3-ethyldimethylamidobenzene, Trans., 420.
Hoeffken, W. D. See Fittig.
Hölzle, R. See Gattermann.
Hoff. See Van't Hoff.
Hoffmann, E., and V. Meyer, benzoyl compounds, 604.
—— —— first product of the reduction of nitro-compounds with tin and hydrochloric acid or stannous chloride, 291.
Hoffmann, O., nitrosonaphtholsulphonic acids, 346.
Hoffmeister, W., cellulose-gum, 129.
Hoffmeyer, H. See Meyer.
Hofmann, A. W. v., polymeric methylthiocarbimide, 798.

Hofmann, A. W. v., and S. Gabriel, action of iodine on thiobenzamide, 1109.
Hofmann, A. W. v., and F. Mahla, diethyldithiophosphinic acid, 1422.
Hofmeister, F., crystalline egg albumin, 515.
Hofmeister, F. See also Ellenberger.
Hogg, T. W., estimation of chromium in steel, 538.
Holland, R. J., alteration of the conductivity of a solution by the addition of a small quantity of a non-electrolyte, 1382.
Holle, O., tertiary phosphines and arsines, 984.
Hollemann, A. F., constitution of mercuric fulminate, 25.
—— dinitrosacyls, 971.
—— isonitrosoanilacetone, 985.
—— testing the purity of platinic chloride, 1526.
Hollemann, A. F. See also De Vries.
Holst, A. See Otto.
Holt, A., stereometric relations of erucic and brassidic acids, 429, 812, 1427.
Hoogewerff, S., and W. A. Van Dorp, γ-amidoquinoline, 725.
Hooker, S. C., the constitution of "lapachic acid" (lapachol) and its derivatives, TRANS., 611.
Hooper, D., mineral substance in teak, 230.
Hopkins, F. G. See Starling.
Hoppe-Seyler, colorimetric estimation of hæmoglobin, 1264.
Hoppe-Seyler, F., extraction of the dissolved gases in water, 1526.
Hoppe-Seyler, G., new test for sugar in urine, 1529.
Horbaczewski, J., formation of uric acid from nucleïn, 646.
Houdas, J., digitaleïne, 222.
Hough, O., iodation of parabromobenzoic acid: salts of parabromometanitrobenzoic acid, 714.
Howell, E. E., new meteorites, 1413.
Howitz, H. See Claus.
Huber, A., physiological action of dinitrobenzene, 366.
Hugounenq, L., influence of wine on peptic digestion, 87.
Hunt, A. E., G. H. Clapp, and J. O. Handy, analysis of aluminium, 1130.
Hunt, T. S., natural classification of minerals, 415.
Hunter, M., and H. Rosenbusch, monchiquite, a rock of the elæolite-syenite class, 1058.
Huntington, O. W., the prehistoric and Kiowa Co. pallasites, 1059.
Huppert, Hamburger's method of estimating small quantities of iron, 1525.
Huston, H. A., action of ammonium citrate on high-grade aluminium phosphate, 1127.

I.

Iddings, J. P., and S. L. Penfield, minerals in hollow spherulites of rhyolite, 23.
Igelström, L. J., jacobsite and braunite from Sweden, 1404.
Ikuta, M., action of ethyl acetoacetate on quinone. Synthesis of benzofurfuran derivatives, 608.
Immendorff, H., the nitrogen question, 374.
Immerheiser, C. See Medicus.
Ingle, H. See Smithells.
Inoko, toxic principle of *Amanita pantherina*, 232.
Isaac, J. F. V., acetic acid from cellulose and other carbohydrates. Lignocellulose and ferric ferricyanide, 1421.
Istel, E., indulines, 492.
Istrati and Edeleanu, action of acetic anhydride on glucose, 1293.
Istrati and Georgescu, iodobenzene, 1310.

J.

Jablin-Gonnet, action of benzyl chloride on unsymmetrical metaxylidine, 314, 1320.
Jackson, C. L., and W. B. Bentley, products of the action of nitric acid on ethyl bromotrinitrophenylmalonate, 1217.
—— tribromonitrobenzene, 1182.
Jacobson, J., unorganised ferments, 899.
Jacobson, P., and W. Fischer, reduction products of azo-compounds, 839.
Jäger, G., stochiometry of solutions, 1382.
Jaffa, M. E., composition of the ramie plant (*Boehmeria*), 1511.
Jahns, E., alkaloïds of the areca nut, 737.
Jahoda, R. See Goldschmiedt.
Jaksch, R. v., peptone in the blood and organs of leucæmic patients, 519.
Jandrier, E., nitro-derivative of antipyrine, 730.
Janeček, G., sensitiveness of the hæmatin spectrum and the formation

of hæmin crystals as proof of the presence of blood, 1369.
Jannasch, P., and K. Aschoff, analysis of galena, 662.
—— —— estimation of sulphur in galena and minerals containing lead, 658.
Jannasch, P., and T. Bickes, analysis of galena, 663.
Jannasch, P., and P. Etz, separation of the metals of the hydrogen sulphide group by means of bromine vapour, 385, 540, 754.
Jannasch, P., and C. J. Franzek, separation of manganese, nickel, and cobalt, 240.
Jannasch, P., and R. Niederhofheim, separation of metals in alkaline solution by hydrogen peroxide, 537.
Jannasch, P., and H. Vogtherr, decomposition of chrome iron ore by hydrochloric acid under pressure, 210.
Jannasch, P., and V. Wasowicz, estimation of sulphur in inorganic sulphides. Analysis of molybdenite, realgar, and orpiment, 657.
Jansen, R. See Gabriel.
Jean, F., estimation of glycerol, astringent acids, and colouring matter in wine, 246.
Jeanprêtre, J. See Michaël.
Jenckel, L. See Wallach.
Jenisch, K. See Pechmann.
Joachim, J. See Claus.
Joannis, action of sodammonium and potassammonium on metals, 275.
—— definite alloys of sodium, 773.
Jörgensen, S. M., constitution of cobalt, chromium, and rhodium bases, 783.
—— roseochromium salts, 782.
Johnson, E. S. See Gattermann.
Johnson, G. S., reducing agents in normal human urine, 1504.
Johnson, W. See Wanklyn.
Johnstone, A., action of water on mica, 573.
Johnstone, M., fertility of heavy loam increased by lime, 523.
Johnstone, W., estimation of glycerol by alkaline permanganate, 544.
Johnstone, W. See also Wanklyn.
Joly, A., action of light on ruthenium peroxide, 282.
—— ruthenium chloride and hydroxychloride, 688.
—— saline compounds of the lower ruthenium oxides with the higher oxides, 282.
Joly, J., determination of the melting point of minerals, 414.
Jolyet, F., and C. Sigalas, dissolved nitrogen in blood, 1257.
Jones, H. C., the volumetric estimation of mercury, Trans., 364.
Jones, H. C. See Morse.
Jones, J., decomposition of minerals containing titanium, 664.
Jones, R., analysis of phosphates, 99.
Jorissen, A., and E. Hairs, linamarin, 502.
Josephy, W. See Freund.
Joslin, E. P. See Chittenden.
Jüptner, H. v., Wiborgh's gasometric method for the estimation of carbon in iron, 1030.
Juillard, P., Turkey-red oil, 819.
Juillard and Curchod, depression of the melting point by phenol, 555.
Jungfleisch, E., and E. Leger, apocinchonine and diapocinchonine, 1253.
—— —— isochinchonines, 222.
Junghahn, A. See Reissert.

K.

Kachler, J., behaviour of the silver salts of organic acids on dry distillation, 37.
Kakuchi, Y., cordierite as contact mineral, 1056.
Kalecsinszky, A., helvine from Hungary, 1412.
Kanonnikoff, A. A., specific rotatory power of tartaric acid and its salts, 1308.
Karau, G., tetravinylpyridine, 1483.
Karau, G. See also Ladenburg.
Karchowski, D. v. See Töhl.
Karstens, H. See Krafft.
Kaufmann, H. See Nietzki, Witt.
Kauthack, A. A., cobra poison, 1118.
Kayser, W., and A. Reissert, julole, 883.
Kehrer, E. A., condensation of levulinic acid with furfuraldehyde, 442.
Kehrmann, F., dinitrosoazobenzene, 1198.
—— thymol, 1078.
Kehrmann, F., and M. Freinkel, complex inorganic acids: phosphotungstic acids, 1160.
Kehrmann, F., and J. Messinger, azonium compounds, 1108.
—— —— nomenclature of rings consisting of two carbon and three nitrogen atoms, 889.
—— —— so-called dinitrosoazobenzene, 889.
Keiser, E. H., silver and copper compounds of acetylene, 1416.
Kekulé, A., formaldehyde, 1423.
Keller, H. F. See Lane.

Kellner, O., H. Sakano, D. Sato, and S. Shinjo, action of lime as a manure, with special regard to paddy fields, 93.
Kenna. See Mc Kenna.
Kenngott, A., formula of axinite, 125.
—— formula of tourmaline, 1410.
—— formulæ of Vesuvian minerals, 417.
Keppler, F., and V. Meyer, 1 : 3-dinitropropane, 1061, 1415.
Kerrow. See Mac Kerrow.
Kerry, R., and S. Fraenkel, action of the bacillus of malignant œdema on carbohydrates and on lactic acid, 91.
Kestner. See Scheurer-Kestner.
Kiliani, H., digitalin, 1482.
—— digitalonic acid, 1241.
—— digitonin, 501.
—— preparation of digitogenin, 1483.
Kimball, J. P., genesis of iron ores by replacement of limestone, 126.
Kinzel, W., oxidation products of paramidophenetoïl, 158.
Kipping, F. S., formation of a hydrocarbon, $C_{18}H_{12}$, from phenylpropionic acid, Proc., **1892**, 107.
Kipping, F. S. See also Armstrong.
Kirchner, L., phenyllutidinedicarboxylic acid and phenyllupetidinedicarboxylic acid, 1486.
Kirkaldy, P. H., urea oxalate, 1421.
Kirman, W. See Thorpe.
Kirpal, A., first product of the reduction of nitro-compounds with stannous chloride, 1067.
Kisch, W., estimation of free oxygen dissolved in water, 98.
Kisel, I., action of methyl iodide and of chloroform on nitroisopropane, 1290.
Kislakowsky, E. D., meteorite of Turgaisk, 418.
Kitschelt, M. See Bamberger.
Kitt, M. See Strache.
Kleber, C. See Stohmann.
Kleinstück, O., sp. gr. of Japan wax, 428.
Klett, M. See Baumann, Busch.
Klingemann, F., action of phenylhydrazine on unsaturated γ-di-ketones, 995.
—— desylacetic acid, 1002.
—— is alcohol eliminated by the milk ?, 365.
Klingemann, F. See also Laycock.
Klobb, P., crystallised anhydrous sulphates, 941.
Klobb, T., mineralising influence of ammonium sulphate, 1399.
Klüss, K. See Fock.
Knoevenagel, E. See Chalany.
Knorr, L., acetoacetanilide, 708.
Knorr, L., and P. Duden, pyrazole derivatives, 731.
Knorr, L., and H. Taufkirch, β-methylamidocrotononanilide, 709.
Kobert, R., cyanmethæmoglobin and detection of hydrogen cyanide, 361.
Kobert, R. See also Kruskal.
Koch, K. R., and A. Wüllner, galvanic polarisation at small electrodes, 759.
Kochs, E. See Fittig.
Köbner, E. See Auwers.
Koefoed, E., acids of butter, 1113.
König, E. See Behrend.
König, G., oxidation products of mercapturic acids, 1090.
Koenig, G. A., paramelaconite and footeite, 415.
König, J., Schützenberger's process for the estimation of free oxygen, 98.
Koenigs, W., condensation of chloral with ketones, 694.
—— dry distillation of organic silver salts, 293.
Koenigs, W., and R. W. Carl, condensation of isoamylene and cinnamene with phenols, 446.
Koenigs, W., and A. Eppens, camphorone, 626.
Koenigs, W., and C. Mai, condensation of unsaturated hydrocarbons with phenols, 1443.
Koenigs, W. See Busch, Comstock.
Koerner, G., and P. Biginelli, fraxin and fraxetin, 628.
Kohlrausch, F., solubility of glass in cold water, 277.
Kohn, C. A., application of electrolysis to qualitative analysis, 540.
Koller, G., derivatives of paraphenylbenzophenone, 186.
Kondakoff, I., constitution of tiglic and angelic acids, 1304.
Koninck. See De Koninck.
Konovaloff, action of dilute nitric acid on mononaphthene, 443.
—— nitration of hydrocarbons of the methane series, 575.
Kopp, K., substitution products of stilbene and thionessal, 718.
Kornauth, C., and A. Archc, metabolism in pigs fed with corn cockle, 1018.
Kornblum, H., excretion of nitrogen in kidney disease, 743.
Kossel, A., derivatives of phenylamidoacetic acid, 467.
Kossel, A. See also Bruhns.
Kostanecki, S. v., xanthones and hydroxyxanthones of the naphthalene and quinoline series, 1098.
Kostanecki, S. v., and B. Nessler, hydroxyxanthones, 504.

Kostanecki, S. v., and R. Rutishauser, hydroxyxanthones, 1096.
Kostanecki, S. v., and S. Seidmann, bye-products in the preparation of hydroxyxanthones, 1097.
Kostanecki, S. v. See also Ganelin.
Kothe, R., alkyl derivatives of hydroxylamine, 316.
Kouklin, E., action of potassium sulphate on strontium carbonate, 1276.
Kowalski, M., hydroxyquinones, 45, 1098.
Koydl, T., precipitation of raffinose by ammoniacal lead acetate, 1294.
Kozai, Y., preparation of teas, 1371.
Krabbe, G., diastase, 92.
Kraemer, G., and A. Spilker, condensation products of allyl alcohol with methylbenzenes, 156.
Krafft, F., and A. Beddies, action of bromine on the higher fatty acids, 695.
Krafft, F., and E. Bourgeois, imidosulphonic acids, 700.
Krafft, F., and H. Karstens, diparatoluamide and diorthotoluamide, 712.
Krafft, F., and L. Reuter, higher homologues of acetylene, 1163.
Krafft, F., and A. Roos, alkyl salts of sulphonic acids, 1219.
Krafft, F. See also Eitner, Hantzsch, Phookan.
Kraft, G. See Pictet.
Kraus, A., action of nitrous acid on resorcinol diethyl ether and on triethylresorcinol, 44.
Kraus, G., calcium oxalate in the bark of trees, 1370.
Kraut, K. See Goldberg.
Krecke, F. See Paal.
Kremers, E., citronellic aldehyde, 1068.
Kremers, E. See also Sieker.
Kresling, K., pollen of *Pinus sylvestris*, 232.
Kretzschmar, M., commercial assay of alums, 535.
Kreusler, U., direct combination of chlorine with metals, 401.
Kritschenko. See Petrenko-Kritschenko.
Krohl, P., action of oxalic acid and its derivatives on the animal economy, 1019.
Kronstein, A., preparation of symmetrical tribromhydrin, 577.
Krüger, M., adenine, 219, 890.
—— estimation of small quantities of calcium, 914.
Krüger, T. R. See Drechsel.
Krug, W. H., estimation of iron and aluminium in the presence of phosphoric acid, 755.
Kruskal, N., and R. Kobert, *Agrostemma githago* (corn cockle), 370.
Kubel, action of magnesium acetate on magnesium oxide and on lead oxide, 1178.
Kubel, W., analysis of Carlsbad salt, 659.
Kubierschky, K. See Feit.
Kühling, O., alloxan hydrazones, 442.
—— azines of the uric acid group, 70.
Kühn, B., and J. Riesenfeld, action of carbonyl chloride on benzylamine, 312.
Kümmel, G., separation of precipitates at the boundary of electrolytes, 1038.
Küster, F. W., freezing point of isomorphous mixtures, 396.
Kuntzmann, M., preparation of cuprous acetylide, 421.
Kunz, G. F., brookite, octahedrite, quartz, and ruby, 1055.
—— meteoric iron from Colfax township, North Carolina, 1059.
—— meteoric iron from Ferguson, North Carolina, 1059.
Kunz, G. F., and E. Weinschenk, aërolite from Kansas, 795.
Kunz, P. See Goldberg.
Kuriloff, B., terpenes from the resin of *Pinus abies*, 625.
Kuriloff, V., action of hydrogen peroxide on the hydrated oxides of cadmium, zinc, and magnesium, 1278.
Kurnakow, N., silver compound of thiocarbamide, 441.
Kurtenacker, L. See Nietzki.
Kwasnik, H., action of barium peroxide on metallic salts, 408.
Kwasnik, W., action of ammonia on cadmium chloride, 566.
—— crystalline constituent of *Genipa brasiliensis*, 1509.
—— kuromoji oil, 1480.
Kwisda, A., action of hydriodic acid on amido-acids, 38.

L.

Laborde, J. V., physiological action of strontium salts, 227.
Lachaud, M., and C. Lepierre, analysis of chrome-yellow, 663.
—— —— lead chromate, 567.
—— —— new iron salts, 943.
—— —— thallium chromate, 567.
Lachaud, M. See also Lepierre.
Lachowicz, B., dissociation of ferric phosphate in presence of water and of saline solutions, 1282.

Lacroix, A., fouqueite, a new mineral, 1056.
Ladenburg, A., dimethyldipiperidyl, 1487.
—— hyoscine, 1366.
—— nipecotinic acid, 1485.
—— piperidinecarboxylic acids, 1486.
Ladenburg A., and G. Karau, isonipecotinic acid, 1486.
Lafont, J. See Bouchardat.
Lagai, G., ethoxyphenylsulphonic acids, 1089.
Lagodzinski, K. See Graebe.
Lainer, A., estimation of silver and gold by means of hydroxylamine hydrochloride, 662.
Lamb, T. See Bailey.
Lampe, O. See Michaelis.
Landolt, H., junr., action of halogens on chloranilic and bromanilic acids, 834.
Landsteiner, K., influence of nutrition on the composition of blood ash, 225.
Landsteiner, K. See also Fischer.
Lane, A. C., H. F. Keller, and F. F. Sharpless, chloritoïd, grünerite, and riebeckite from Michigan, 793.
Lang, H. See Curtius.
Lang, W., oxalylorthamidophenyl mercaptan and oxalylorthamido-α-naphthyl mercaptan, 1079.
Langbein, H. See Stohmann.
Lange, K., and A. Zufall, new method for the preparation of some aromatic nitro-ketones, 1459.
Langermann, G., estimation of hydrochloric acid in the contents of the stomach, 1125.
Langlet, N. A., action of β-iodopropionic acid on ethyl thiocarbamate, 440.
Langlois, P., physiological action of nickel carbon oxide, 365.
Lapicque, L., colorimetric estimation of iron, 240.
Laspeyres, H., polydymite, ullmanite, and wolfsbergite, 124.
Lassar-Cohn, cholic acid and dehydrocholic acid, 741.
—— presence of myristic acid in ox gall, 1114, 1503.
Latten, M. See Zincke.
Lauder, A. See Dobbie.
Lauenstein, C., viscosity of aqueous salt solutions, 1044.
Laurent, E. See Schloesing.
Lauth, C., diamidosulphobenzide and its derivatives, 1093.
—— metadiamidotetramethylbenzidine, 1222.
—— oxidation of azo-compounds, 48.
Lauth, C., preparation of β-alizarinamide, 864.
Lavenir, A., martite, 1055.
Laves, E., chemical and physiological relations of sulphones, 153.
—— formation of trisulphones from disulphones, 613.
—— sulphones, 850.
—— trithiorthoformates, 611.
Lawes, Sir J. B., and J. H. Gilbert, sources of nitrogen of our leguminous crops, 367.
Laycock, W. F., and F. Klingemann, an examination of the products obtained by the dry distillation of bran with lime, Proc, 1892, 138.
Lazareff, Miss P., displacement of hydrogen by haloïds in aromatic hydrocarbons, 1310.
—— mutual displacement of haloïds, 1270.
Lea, M. C., allotropic silver, 116.
—— allotropic silver. III. Blue silver, 15.
Lean, B., and W. A. Bone, behaviour of ethylene on explosion with less than its own volume of oxygen, Trans., 873.
Le Bel, J. A., rotatory power of diacetyltartaric derivatives, 669.
Lecco, M. T., estimation of glycerol in sweet wines, 1263.
Lechartier, G., composition and cultivation of the Jerusalem artichoke, 1024.
Le Chatelier, H., equilibrium of chemical systems under unequal pressures, 937.
—— metallic borates, 404.
—— optical measurement of high temperatures, 761.
—— reproduction of acid rocks, 23.
—— second law of thermodynamics, and its application to chemical phenomena, 3.
Ledent, M. See De Koninck.
Lederer, L., amido- and methamidocrotonanilide, 965.
—— nomenclature of pyrazolones, 1004.
—— synthesis of pyrazolone derivatives, 634.
Leduc, A., atomic weight of oxygen, 1388.
—— composition of water and Gay-Lussac's law of volumes, 1271.
—— dilatation of phosphorus, and its change of volume at the melting point, 7.
Leent. See Van Leent.
Leffmann, H., and W. Beam, estimation of fat in milk, 1532.

Leger, E. See Jungfleisch.
Lehmann, O., artificial colouring of crystals, 269.
—— spheres of condensation and evaporation, 1149.
Lellmann, E., affinity coefficients of acids, 1269.
—— metachloroparacetotoluidide, 450.
Lellmann, E., and B. Arnold, intramolecular formation of an azo-group, 316.
—— —— substance containing a ring of 18 members, 890.
Lellmann, E., and J. Schliemann, affinity coefficients of acids, 1269.
Lendrich, K., constituents of *Meniantheș trifoliata* and of *Erythræa centaurium*, 1262.
Leonardi, A. See Mazzara.
Leone, T., and O. Magnanini, nitrification of organic nitrogen, 367.
Lepierre, C., and M. Lachaud, nickel and cobalt, 1282.
Lepierre, C. See also Lachaud.
Lépine, R., formation of sugar from peptones in blood, 1502.
Lépine, R., and Barral, glycolytic power of blood and artificial production of diabetes, 364.
—— —— hematic glycolysis: estimation of glycogen in the blood, 89.
—— —— variations of the glycolytic and saccharific power of blood in diseases, 517.
Leprince, cascarin, 1483.
Leroy, J. A., action of phosphoric chloride on methyl naphthyl ketones, 495.
Lesage, P., quantity of starch in the tubercles of the radish, 92.
—— sodium chloride in plants, 651.
Lespieau, R., dibromopropylene, 420.
—— picene, 623.
Leteur, stannibromides, 121.
Lewes, V. B., analysis of the products of incomplete combustion, 407.
—— the luminosity of coal-gas flames, Trans., 322.
—— the origin of acetylene in flames, Proc., **1892**, 47.
Lewkowitsch, J., estimation of cholesterol, 544.
Lezé and Allard, estimation of fat in the products from milk, 391.
Lieben, A., dry distillation of silver salts of organic acids, 811.
—— errors arising in chemical operations owing to the employment of gas flames, 1374.
—— preparation of crotonaldehyde, 1424.
Liebermann, C., heat evolved in the isomeric change of the oxime of opianic anhydride, 459.
Liebermann, C., stereoisomeric and polymeric cinnamic acids, 469.
Liebermann, C., and F. Damerow, silver phenylacetylide, 831.
Liebermann, C., and F. Dickhuth, acetylhydrindigotin and acetylindigo, 480.
Liebermann, C., and A. Hartmann, condensation of cinnamic acid with hydrocarbons, 1228.
—— —— condensation of cinnamic and allocinnamic acids, 848.
Liebermann, C., and L. Limpach, ψ-tropine and some ψ-tropeïnes, 891.
Liebermann, C., and H. Sachse, diiodocinnamic acid, 470.
Liebermann, C., and W. Scholz, formation of allocinnamic acid from phenylpropiolic acid, 848.
Liebig, cause of the rapid curdling of milk during thunderstorms, 1370.
Liechti, P. R., rind of *Garzinia mangostana*, 205.
Limpach, L., synthesis of the sixth dihydroxytoluene, 447.
Limpach, L. See also Conrad, Hodgkinson, Liebermann.
Limpricht, H., preparation of nitrososulphonic acids, 475.
Limpricht, H., and F. Meyer, azobenzene-, hydrazobenzene-, and benzidine-disulphonamides, 973.
Linder, S. E., and H. Picton, some metallic hydrosulphides, Trans., 114.
Linder, S. E. See also Picton.
Lindgren, W., analcime as a rock-forming mineral, 1413.
Lindgren, W. See also Melville.
Lindsey, J. B., and B. Tollens, dextrose from sulphite-cellulose and from fir wood, 801.
—— —— so-called artificial pectic acid from fir wood, 827.
—— —— wood-sulphite liquor and lignin, 802.
Linebarger, C. E., formation of layers in solutions of salts in mixtures of water and organic liquids, 1146.
—— hydroxyanthranol, 346.
—— nature of colloïd solutions, 766.
—— reaction between benzene and benzal chloride in presence of aluminium chloride, 719.
—— reaction between triphenylmethane and chloroform in presence of aluminium chloride, 722.
Ling, A. R., studies on isomeric change. No. IV. Halogen derivatives of quinone. Part I, Trans., 558.

Ling, A. R., and J. L. Baker, halogen derivatives of quinone. Part II. Trans., 589.
Link, C., berberine and hydroberberine, 1498.
Linossier, G., resolution of inactive lactic acid by *Penicillium glaucum*, 297.
Lintner, C. J., isomaltose, 1293.
Lipp, A., 1-methyl-Δ^2-tetrahydro-2-hydroxyethylpyridine, 1244.
—— synthesis of tetrahydropyridine derivatives, and their conversion into piperidine derivatives, 1243.
Lippmann, E., preparation of homologues of quinine, 222.
Lippmann, E., and F. Fleissner, action of hydriodic acid on cinchonine, 639.
—— —— action of hydriodic acid on quinine: isoquinine, 81.
—— —— the hydriodo-compounds of the cinchona alkaloïds, 1363.
Lippmann, E. O. v., organic acids in beet juice, 231.
Lippmann, F., constitution of allyl cyanide, 27.
Lobry de Bruyn, C. A., apparatus for determining vapour pressures, 679.
—— displacement of the nitro-group by chlorine or bromine, 305.
—— estimation of sulphur in red copper, 753.
—— explosion of ammonium nitrate, 683.
—— hydroxylamine, 402, 1391.
Lobry de Bruyn, C. A., and F. H. Van Leent, estimation of copper, 753.
Loczka, J., Hungarian minerals, 1054.
Loeb, W. See Pulvermacher.
Lösekann, G., formaldehyde, 423.
Löw, M., ethylation of salicylaldehyde, 57.
Loew, O., action of azoimide on living organisms, 90.
—— influence of phosphoric acid on the formation of chlorophyll, 1261, 1372.
Loewenherz, R., asymmetrical amidoisophthalic acid, 1464.
—— dimetaditolyl, 852.
Lorentz, G. See Wallach.
Lorenzen, J. See Bamberger.
Losanitsch, S. M., aromatic dithiocarbamates, 55.
—— meteorite of Jelica, 795.
Lossen, W., amidines, 51.
—— constitution of the hydroxamic acids, 461.
—— decomposition of glutaric acid at a high temperature, 297.
Lossen, W., so-called physically isomeric hydroxylamine derivatives, 711.
Lossen, W., and C. Rahnenführer, composition and crystalline form of barium isophthalate, 179.
Lossen, W., and G. Voss, metallic formates, 140.
Louise, E., and Perrier, metallic compounds of aromatic ketones, 1205.
Lucchesi, A. See Antony.
Luckow, C., volumetric estimations and separations by means of potassium ferrocyanide and ferricyanide, 1129, 1527.
Ludwig, E., action of sulphuric acid on methylethylacraldehyde, 951.
Luedecke, O., heintzite, 791.
Luedeking, C., synthesis of crocoïte and phœnicocroïte, 792.
Luedeking, C., and H. A. Wheeler, barytes from Missouri, 792.
Lukjanow, S. M., bile during inanition, 225.
Lumsden, J. S. See Frankland.
Lunge, G., action of certain liquids on aluminium, 687.
—— analysis of sodium nitrite, 1029.
—— gasvolumetric analysis, 538.
—— improvement in gasvolumetric apparatus, 524.
—— levelling instrument for gasometric work, 400.
—— the gas-volumeter and gravivolumeter, Proc., **1891**, 168, 170.
—— volumetric estimation of alumina, 535.
Lunge, G., and L. Marchlewski, new apparatus for the estimation of combined or free carbonic acid, 531.
—— —— revised hydrochloric acid tables, 11.
Lunge, G., and H. Rey, revised nitric acid tables, 13.
Lungo. See Del Lungo.
Lusk, G. See Voit.
Luzi, W., allotropism of amorphous carbon, 945.
—— artificial corrosion of the diamond, 1394.
—— carbon, 565.
—— graphite, 406.
Luzzato, G., natrolite from Monte Baldo, 690.
Lyons, R. E. See Van Nüys.

M.

McBryde, J. B., chemical study of the cotton plant. Feeding value of the cotton plant, 1510.

McCauley, A. W. See Smith.
McCay, L. W., separation of thioarsenic and thioxyarsenic acids, 1519.
—— test for chromium, 1133.
McGowan, G., the iodometric estimation of chloric acid in chlorates, Trans., 87.
MacGregor, J. See Frankland.
McKenna, A. G. See Drown.
Mackenzie, J. E., and W. H. Perkin, jun., synthesis of hexahydroterephthalic acid, Trans., 172.
Mackenzie, J. E. See also Perkin.
MacKerrow, W., bromine carriers, 155.
Macnair, D. S., detection of chlorine and bromine in the presence of iodine, 1514.
MacWilliam, J. A., salicylsulphonic acid as a test for albumoses and peptones, 552.
Magnanini, G., absorbent power of coloured salts and electrolytic dissociation, 757.
—— catalytic influence of acids on the velocity of the reaction between hydrogen peroxide and hydriodic acid, 110.
—— freezing points of aqueous solutions of boric acid and mannitol, 263.
—— influence of boric acid on the electrical conductivity of aqueous solutions of organic acids, 256.
—— influence of boric acid on the electrical conductivity of dilute alcoholic solutions of organic acids, 1265.
Magnanini, G., and M. Scheidt, action of phenylhydrazine and hydroxylamine on dehydrodiacetyllevulinic acid, 1429.
Magnanini, O. See also Leone.
Mahla, F. See Hofmann.
Mahler, P., calorimetry, 260.
—— distillation of coal, 395.
Mai, C. See Koenigs.
Mai, J., action of diazo-compounds on oximes, 163, 1079.
—— action of hydroxylamine on diazobenzene and paradiazotoluene chlorides, 710.
—— compounds of sulphur and phosphorus, 14.
Mai, J., and K. Aschoff, preparation of collidine, 725.
Malbot, H., and A. Malbot, action of allyl iodide on trimethylamine: trimethylallylammonium iodide, 1295.
—— —— action of capryl iodide on trimethylamine, 806.
—— —— action of isoamyl iodide on trimethylamine, 805.
Malbot, H., and A. Malbot, action of isobutyl iodide on trimethylamine, 805.
—— —— action of isopropyl iodide on trimethylamine: trimethylisopropylammonium iodide, 1295.
—— —— action of propyl iodide on trimethylamine: trimethylpropylammonium iodide, 1294.
—— —— formation of tetralkylammonium iodides, 133.
Malfatti, H., nucleïns, 224, 1501.
Mallard, native iron from Cañon Diablo, 947.
Mallard and E. Cumenge, boléite, 123.
Malot, C., estimation of phosphorus in iron and steel, 528.
Mangold, C., analysis of beeswax, 1034.
Mangold, K., stereochemistry of trihydroxystearic acids, prepared from ricinoleïc acid and from ricinelaïdic acid, 1304.
Manning, T. D. See Tubby.
Mansbridge, W., new method for the estimation of unsaponifiable matter in fats, 1533.
Manseau, M. H., detection and estimation of santonine, 666.
Maquenne, action of sulphuric acid on hydrocarbons with a closed chain, 967.
—— barium carbide, 685.
—— direct combination of nitrogen with alkaline earth metals, 566.
—— natural synthesis of the vegetable hydrocarbons, 1234.
—— nitrides of barium and strontium, 776.
Maquenne, L., hydrocarbon derived from perseïtol, 1065.
Marcano, V., and A. Muntz, ammonia in the atmosphere and in rain water of the tropics, 381.
Marchesini, G., carbaminethioacetophenone, 1317.
Marchlewski, L., aqueous solutions of tartaric and racemic acids, 964.
—— colour of nitric acid, 113.
Marchelewski, L. See also Lunge.
Marckwald, W., imidazoles and the constitution of glyoxaline, 1326.
Marckwald, W., M. Neumark, and R. Stelzner, hydantoïns and bases derived from them, 149.
Marcus, E., nitrogenous derivatives of some aromatic dihydroxyaldehydes. 317.
Marek, W., expansion of water, 106.
Mares, F., formation of uric acid in mammals, 1257.

Marie, T., monobromocerotic acid, 1302.
Marino-Zuco, F., new alkaloïd from chrysanthemum flowers, 84.
Markovnikoff, V., hydrobenzoic acids, 714.
—— naphthenes and polymethylenes, 1310.
—— naphthenes and their derivatives in the general system of organic compounds, 1182, 1311.
—— tetramethylenedicarboxylic acids, 1306.
Markovsky, G., E.M.F. of gas batteries, 393.
Marsenille. See Van Marsenille.
Martin. See De St. Martin.
Martin, S., anthrax in man, 1117.
—— chemical pathology of diphtheria, anthrax, and infective endocarditis, 744.
Martina, G., metallic derivatives of phenylhydrazine, 1454.
Mason, W. P., carbazole method for the estimation of nitrates in water analysis, 243.
Massan, C. See Claus.
Massol, G., citric acid, 763.
—— dibromomalonic acid, 1140.
—— glutaric acid, 1141.
—— heat of formation of potassium tricarballylates, 762.
—— tartronic acid and alkali tartronates, 675.
—— thermal constants of active malic acid and potassium and sodium malates, 260.
—— thermochemistry of bibasic organic acids, 395.
—— thermochemistry of bibasic organic acids: methylmalonic and methylsuccinic acids, 1140.
Matignon, C., characteristic difference between alcohol radicles united directly with carbon or with nitrogen, 106.
—— substitution of radicles in union with carbon and nitrogen respectively: explosives, 1141.
—— thermochemistry of guanidine and nitroguanidine, 1142.
Matignon. See also Berthelot.
Matthews, F. E., action of sulphuric acid on the α- and β-modifications of monochlorobenzene hexachloride, Trans., 103.
Mattirolo, E., breithauptite from Sarrabus, Sardinia, 790.
Maxwell, W., choline and betaïne in cotton seed foods, 380.
Mayer, E. See Fittig.
Mayer, R., pyridinecarboxylic acids obtained from berberine, 1357.
Mazzara, G., bromamidocarvacrol, 595.
Mazzara, G., and A. Leonardi, carbazole, 616.
Mazzara, G., and G. Plancher, bromo-derivatives of carvacrol, 156.
—— —— derivatives of carvacrol, 309.
Meara, F. S. See Chittenden.
Medicus, L., estimation of lead, 1522.
Medicus, L., and C Immerheiser, fermentability of dextrins, 922.
Meldola, R., and C. H. Desch, some homonuclear tri-derivatives of naphthalene, Trans., 765.
Meldola, R., and E. M. Hawkins, a method for determining the number of NH_2 groups in certain organic bases, Proc., **1892**, 133.
Meldola, R., and F. W. Streatfeild, ethylene derivatives of diazoamidocompounds, Proc., **1892**, 119.
Melikoff, P., and P. Petrenko-Kritschenko, $\alpha\beta$-dimethylglyceric acid from angelic acid, 207.
—— —— derivatives of isocrotonic acid, 295.
Melnikoff, M. P., zoisite from Orenburg, 690.
Melville, W. H., and W. Lindgren, minerals from the Pacific coast, 1407.
Melville, W. H. See also Hillebrand.
Menozzi, A., and G. Appiani, derivatives of glutamic acid, 298.
Menschutkin, N., and M. Vasileff, affinity coefficients of alkyl iodides and bromides, 1289.
Merck, E., subsidiary alkaloïds of belladonna, 1255.
—— terpin hydrate from eucalyptus oil, 1235.
Merling, G., tropine, 358.
Merrill, G. P., and R. L. Packard, azure-blue pyroxenic rock from New Mexico, 1057.
Merz, V., magnesium nitride, 409.
Meslans, M., acetic fluoride, 1068, 1069.
—— fluorhydrins from glycerol, 799.
Mesnard, E., essence of sandal wood, 1379.
Messinger, J. See Kehrmann.
Meunier, J., reduction of benzene hexachloride, 594.
Meyenburg, F. v. See Auwers.
Meyer, E. v. polymerisation of the nitriles, 576.
Meyer, F. See Limpricht.
Meyer, R., and H. Hoffmeyer, fluoresceïn, 970.
—— —— the fluoresceïn group, 1228.

Meyer, T., estimation of iron and alumina in phosphates, 536.
Meyer, V., aliphatic nitro-compounds, 575.
—— commercial benzoic chloride, 604.
—— lecture experiments on oxyhydrogen gas, 562.
Meyer, V., and F. Müller, substitution in the aliphatic series, 577, 1414.
Meyer, V., and W. Wachter, iodosobenzoic acid, 1460.
Meyer, V., and H. Wege, new method of formation of desaurins, 340.
Meyer, V. See also Askenasy, Auwers, Cathcart, Dittrich, Freyer, Heidenreich, Hoffmann, and Keppler.
Meyerhoffer, W., interval of change, 1145.
Michael, A., action of zinc on ethyl dibromosuccinate, 40.
—— constitution of ethyl sodacetoacetate, 1178, 1428.
Michael, A., and O. Schulthess, additive products of ethyl sodacetoacetate and sodiomalonate with ethereal salts of unsaturated acids, 590.
Michaël, H. A., and J. Jeanprêtre, formation of aromatic nitriles, 1094.
—— —— mandelic acid and its nitrile, 1088.
Michaelis, A., inorganic derivatives of phenylhydrazine, 1324.
Michaelis, A., and R. Burmeister, ethyl malonate phenylhydrazide and 1-phenyl-3 : 5-pyrazolidone, 1004.
Michaelis, A., and R. Hermens, β-succinylphenylhydrazide : 1-phenyl-3 : 6-orthopiperazone, 1494.
Michaelis, A., and O. Lampe, synthesis of phenylpyrazolidine, 355.
Michaelis, A., and F. Oster, action of the chlorides of phosphorus, arsenic, boron, and silicon on aromatic hydrazines, 1324.
Michaelis, A., and J. Rabinerson, action of arsenious chloride on tertiary aromatic amines, 1321.
Michaelis, A., and F. Rothe, aromatic phosphorus compounds, 1084.
Michaelis, A., and J. Ruhl, thionyl chloride and aromatic hydrazines, 1324.
Michaelis, L., nicotenylamidoxime, 206.
Michaud, G., sapotin, a glucoside, 724.
Michel, O. See Grandmougin.
Micko, C., separation of malic acid from succinic and tartaric acids, 1531.
Miersch, W., formation of hydrindone derivatives from halogen cinnamic acids, 1222.
Miller, A. K., interaction of bromine and toluene : preparation and properties of ortho- and para-bromotoluene and of the dibromotoluenes derivable therefrom : ortho- and para-bromotoluenesulphonic acids, Trans., 1023.
Miller, A. K. See also Thorpe.
Miller, W. v., synthesis of quinaldine, 1245.
Miller, W. v., J. Plöchl, and others, Schiff's bases, 1189.
Miller, W. v., and G. Rohde, phenylhydrindone, 1220.
—— —— α-phenylhydrocinnamic acid, 1211.
Minguin, J., action of sodium benzyloxide on ethyl camphocarboxylate, 74.
—— methyl camphocarboxylates, methylcamphor, and azo-derivatives of cyanocamphor, 1343.
Mintz, N. See Bischoff.
Minunni, G., isomerism of oximes, 291.
Miolati, A., melting points of mixtures, 1139.
—— new method of preparing fatty hydroxamic acids, 698.
Miolati, A. See also Hantzsch.
Mischel, E. See Rügheimer.
Mittelmeier, H. See Scheibler.
Mixter, W. G., decomposition of ethereal nitrates by alkaline solutions, 692.
Modeen, H., action of hydroxylamine on ethyl cyanacetate, 139.
Möhlau, R., oxazine dyes, 887.
Möllenhoff, C., methylphenylpyrazolone and its derivatives, 1245.
Mörner, C. T., estimation of gallic acid in urine, 904.
—— physiological action of gallic and tannic acids, 904.
Moissan, H., action of fluorine on phosphorus trifluoride, 12.
—— amorphous boron, 681, 1153.
—— boron iodide, 1154.
—— boron pentasulphide, 1394.
—— boron phosphides, 272.
—— boron phosphoiodides, 114.
—— boron trisulphide, 1392.
—— carbon diiodide, 1291.
—— place of fluorine in the classification of the elements, 11.
—— preparation of amorphous boron, 682.
Moissan, H., and H. Gautier, specific gravity of gases, 1267.
Moitessier, J., estimation of creatinine in urine, 1135.
—— influence of muscular work on the elimination of creatinine, 364.

Moitessier, J. See also Bertin Sans.
Moldenhauer, F., estimation of zinc by the ferrocyanide process, 915.
Montemartini, C., action of nitric acid on zinc, 1279.
—— serpentine rock from Borzanasca, 1058.
—— the reaction between nitric acid and metals, 1278, 1402.
Monteverde, N., chlorophyll, 1355.
—— influence of carbohydrates on the accumulation of asparagine in plants, 91.
Moody, G. T., metaxylenesulphonic acids [II], Proc., **1891**, 189.
—— sulphonic acids derived from anisoïls [I], Proc., **1892**, 90.
Moore, B., velocity of reaction in mixtures of isohydric and non-isohydric solutions of acids, 936.
Moore, T., estimation of cobalt in maganese ores, 917.
Morel, J., action of boric acid on germination, 651.
Moritz, E. R., and T. A. Glendinning, diastatic action, Trans., 689.
Morrell, R. S. See Ruhemann.
Morse, H. N., and H. C. Jones, redetermination of the atomic weight of cadmium, 1397.
Morse, H. N., and J. White, transportation of solids in a vacuum by the vapours of metals, 1386.
Moscatelli, R., catechol in the urine of hydrophobic rabbits, 1115.
Moscheles and R. Stelzner, analysis of coffee substitutes, 1534.
Mueller, C., oil of lime seed, 92.
Müller, F. See Brühl, Meyer.
Münster, C. A., garnierite from Norway, 1409.
Müntz, A., ammonia in rain water and in the atmosphere, 909.
Müntz, A., and A. C. Girard, value of animal *débris* as nitrogenous dressing, 96.
Müntz, A. See also Marcano.
Muhe, E. G. See Willgerodt.
Muhr, F. See Smith.
Mulder, E., tartryltartaric acid, 965.
Muller, J. A., occurrence of a tetracarbon aldehyde in a brandy, 810.
—— preparation of crotonaldehyde, 809.
Muller, P. T., action of ethyl salts of unsaturated acids on ethyl sodiocyanacetate, 1181.
Muller, P. T., and J. Hauser, velocity of decomposition of diazo-compounds by water, 768.
Murmann, E., derivatives of α-phenylquinoline, 1003.
Murray, T. S., electrolysis of potassium acetate solutions, Trans., 10.
Mussi, U., the latex of *Ficus carica*, 653.
Muter, J., detection of coco-nut fat in butter, 391.
Myers, W. S. See Collie.
Mylius, F., and F. Foerster, examination of glass for chemical purposes, 411.
—— —— preparation and assaying of pure platinum, 789.

N.

Nagai, W. N., dehydrodiacetylpæonol, 845.
—— pæonol, 58.
Namias, R., estimation of tungsten in rich alloys and in steel, 539.
—— extended employment of arsenious acid in volumetric analysis, 1374.
—— volumetric estimation of iron, 240.
—— volumetric estimation of mercury, 663.
Nasini, R., application of Ketteler's formulæ to optical chemistry, 253.
Nasini, R., and T. Costa, sulphinic derivatives and their analogies with compounds of aromatic amines, 34.
Nasini, R., and V. Villavecchia, specific rotatory power of cane sugar in dilute solutions, 801.
Nasse, O., physiological oxidation, 1018.
Natanson, L., law of thermodynamical coincidence and its application to the theory of solution, 557.
Naumann, A., reconversion of heat into chemical energy by production of water- and carbonic anhydride-generator gas, 673.
Nef, J. U., bivalent carbon, 1438.
—— ethyl acetoacetate, 140.
Negbaur, W., potential differences at the surfaces of contact of very dilute solutions, 671.
—— practical form of the Latimer-Clark standard cell, 669.
—— standard cell for small differences of potential, 670.
Nehring, P. See Beckurts.
Neitzel, E., derivatives of diacetovannillone, 61.
Nernst, W., potential difference of dilute solutions, 671.
—— solubility of mixed crystals, 560.
Nernst, W., and R. Pauli, electromotive activity of the ions, 671.
Nernst, W. See also Tammann.

Nessler, B. See Kostanecki.
Neuberg, O. See Gattermann.
Neudörfer, J. See Benedikt.
Neumann, A. See Gabriel.
Neumann, G., behaviour of copper and of the noble metals towards some gases and vapours, 942.
—— α-orthostannic acid, 412.
Neumann, G., and F. Streintz, behaviour of hydrogen towards lead and other metals, 567.
Neumark, M. See Marckwald.
Neville, F. H. See Heycock.
Newbury, S. B., copper sulphites, 1051.
Newbury, S. B. See also Ornsdorff.
Newth, G. S., lecture experiment: dissociation of phosphonium bromide, 401.
—— preparation of hydrobromic acid, 270.
Nickel, E., graphical chemistry of glass, 1158.
Nicol, W. W. J., mutual solubility of salts in water, 8.
Nicolas, C. See Domergue.
Nicolle. See Cazeneuve.
Niederhofheim, R. See Jannasch.
Niementowski, S. v., anhydro-compounds, 837.
—— α-methylphthalic acid, 607.
Nietzki, R., synthesis of Weselsky's resorcinol-blue, 163.
Nietzki, R., and H. Kaufmann, derivatives of trinitroquinol, 314.
Nietzki, R., and L. Kurtenacker, penta-derivatives of benzene, 596.
Nietzki, R., and B Schündelen, action of dinitrochlorobenzene on polyhydric phenols, 310.
Nihoul, E. See De Koninck.
Nilson, L. F., composition of the Leguminosæ, 521.
—— the lactocrite compared with other methods for estimating fat in milk, 550.
Nissen, C., αβ-dichlorocinnamic acid (phenylpropiolic acid dichloride), 1464.
Nissen, D. See Behrend.
Noelting, E., dyes of the triphenylmethane group, 187.
—— nitration of butyltoluenesulphonic acid and butylxylenesulphonic acid, 718.
Noelting, E., and E. Trautmann, derivatives of the methylquinolines and of metadimethylquinoline, 726.
Nordenskiöld, G., pholidolite, a new mineral, 1408.
Nordenskiöld, O., the Ljungby meteorite, 1060.
Nordenström, G., allanite, from Gyttorp, Sweden, 1409.
Norris, G. L., estimation of manganese in slags and ores, 385.
Noyes, A. A., determination of the electrolytic dissociation of salts by means of solubility experiments, 1143.
Noyes, W. A., dibenzylcarbinamine, 1093.
—— lecture experiment: burning sulphur in oxygen, 679.
Nüys. See Van Nüys.
Nuricsán, J., new method of preparing carbon oxysulphide, 15.
Nussberger, G., stereoisomeric dioximes from ethyl acetoacetate and benzoylacetate, 1175.

O.

Obach, E., specific inductive capacity and latent heat of vaporisation, 258.
Obermayer, F. See Paschkis.
Obermüller, K., estimation of cholesterol, 248.
—— saponification with sodium ethoxide, 139.
Obermüller, P. See Fittig.
Obrégia, A., action of potassium cyanide on halogen derivatives of ketones, 324.
Oddo, G., camphor group, 724.
—— relation between the chemical constitution and physiological action of aromatic compounds, 366.
—— stereochemistry of the camphor group, 724.
Off, H. See Richmond.
Oglialoro, A., and O. Forte, action of hydriodic acid and amorphous phosphorus on picrotin, 349.
O'Neill, C., products from indigo-blue, 991.
Ordonneau, C., cause of acidity of grapes: tartromalic acid, 589.
Ormandy, W. R. See Ewan.
Orndorff, W. R., and M. Cauffman, decomposition of some diazo-compounds of nitronaphthalenes with alcohol, 622.
Orndorff, W. R., and S. B. Newbury, preparation of aldol and crotonaldehyde, 1423.
Osborne, T. B., proteïds of the oat kernel, 1120.
Osborne, T. B. See also Chittenden.
Osmond, F., calorimetric researches on the condition of silicon and of aluminium in cast iron, 19.
Oster, F. See Michaelis.
Ostwald, W., chemical action at a distance, 268.

Ostwald, W., colour of the ions, 1137.
—— polybasic acids, 1145.
—— studies on energetics, 1149.
—— the dissociation of liquid nitrogen peroxide, TRANS., 242.
—— the magnetic rotation of dissolved salts, PROC., **1892**, 12.
O'Sullivan, J., the hydrolytic functions of yeast. Part I, TRANS., 593; Part II, TRANS., 926.
—— the specific rotatory and cupric reducing power of invert sugar and of dextrose obtained from cane sugar by means of invertase, TRANS., 408.
Otto, J. G. See Voit.
Otto, R., and D. Drewes, magnesium lead bromide, 566.
Otto, R., and E. Heydecke, aromatic thiosulphonates, 990.
Otto, R., and A. Holst, ethyl and methyl morphine carbonates, 638.
Otto, R., and A. Rössing, aromatic thiosulphonic acids, 478.
—— —— preparation and properties of Bunte's salt (ethyl thiosulphate), 799.
—— —— tautomerism of sulphinic acids, 623.
Otto, T., synthesis of acetovannillone from guaiacol and acetic acid. 61.
Ouvrard, L., lithium nitride, 565.

P.

Paal, C., indazole derivatives, 67.
—— peptone salts from glutin, 895.
—— unsaturated aliphatic amines, 578.
Paal, C., and A. Bodewig, action of orthonitrobenzyl chloride on phenylhydrazine, 1455.
Paal, C., and A. Heupel, unsaturated fatty amines, 30.
Paal, C., and F. Krecke, methylphenyldihydroquinazoline and its derivatives, 80.
Pabst, T., fruit of *Capsicum annum*, 1263.
Packard, R. L. See Merrill.
Pagliani, S., new method of measuring electromotive force and resistance, 105.
Pagnoul, A., experiments on the growth of wheat in a sterile soil, 909.
Palladin, W., amount of proteïds in green and in etiolated leaves: acquisition of green colour and growth of etiolated leaves, 520.
Palmer, A. W., reduction of symmetrical triamidonitrobenzene, 1198.
Papasogli, G., cotton and its products, 584.
Papendieck, A. See Buchner.
Parker, G. See Fittig.
Parlato, E. See Anschütz.
Parmentier, F., abnormal dissolution: saturated solutions, 1047.
—— aluminium in mineral waters, 1287.
—— chalybeate mineral waters, 1289.
—— flameless incandescence produced by coal-gas, 768.
—— lead chlorosulphide and bromosulphide, 685.
—— preservation of mineral waters, 1162.
Partheil, A. See Schmidt.
Paschen, E., derivatives of orthohomosalicylaldehyde and of orthohomoparahydroxybenzaldehyde, 320.
Paschkis, H., and F. Obermayer, pharmacological investigations of ketones and acetoximes, 1506.
Paschkowetzky, S. See Schall.
Paschkowezky, S., aromatic secondary chlorocarbamides and tetra-substituted carbamides, 164.
—— thiophenylcarbamides, 324.
Passmore, F. W. See Dunstan.
Patein, G., detection of normal carbonate in hydrogen alkali carbonates, 1130.
—— transformation of albumin, 362.
Paternò, E., hot mineral spring at Sclafani, 25.
Pattinson, J., and H. S. Pattinson, estimation of manganese in its ores and alloys, 536.
Paul, T., apparatus for hot filtration, 1150.
Paul, T. See also Beckmann.
Pauli, R. See Nernst.
Pawlewski, B., ethyl chlorocarbonate, 963.
Peacock, J. C., volatile oil from *Aristolochia reticulata*, 70.
Péchard, E., estimation of molybdenum, 917.
—— heat of formation of permolybdic acid, 1383.
—— permolybdates, 1160.
—— permolybdic acid, 1283.
Péchard, E. See also Baubigny.
Pechmann, H. v., constitution of ethyl acetoacetate and of the so-called ethyl formylacetate, 816.
—— ethyl acetonedicarboxylate, 431.
—— introduction of acid radicles into ethyl acetoacetate, 696.
—— preparation of dehydracetic acid, 296.
—— preparation of fatty 1 : 2-diketones, 425.

Pechmann, H. v., and O. Baltzer, α-pyridone, 208.
Pechmann, H. v., and K. Jenisch, action of diazobenzene on acetonedicarboxylic acid, 161.
—— —— action of phenylhydrazine on acetonedicarboxylic acid, 162.
—— —— alkylacetonedicarboxylic acids, 148.
—— —— reduction of acetonedicarboxylic acid, 147.
Pekelharing, C. A., coagulation of the blood, 87.
—— fibrin ferment, 1112.
Pellat, H., electrical behaviour of metals in salt solutions, 393.
Pellizzari, G., nitroguanidine, 579.
—— phenylguanazole, 356.
Pellizzari, G., and D. Tivoli, action of cyanogen chloride on phenylhydrazine, 1323.
Penfield, S. L. See Iddings, Wells.
Penrose, R. A. F., limonite in Texas, 1405.
Peratoner, A., sparteïne, 1362.
Perdrix, L., a bacterium which ferments starch and produces amyl alcohol, 90.
Perkin, A. G., action of nitric acid on oxanilide and similarly constituted substances, Trans., 458.
Perkin, A. G., and J. E. Mackenzie, action of nitric acid on anthracene. Part II, Trans., 865.
Perkin, W. H., sen., on the refractive power of certain organic compounds at different temperatures, Trans., 287.
—— the magnetic rotation of compounds supposed to contain acetyl, or to be of ketonic origin, Trans., 800.
Perkin, W. H., jun., note on a new acid from camphoric acid, Proc., **1892**, 55, 68.
Perkin, W. H., jun., and W. Sinclair, synthetical formation of closed carbon-chains. Part II (*cont.*): derivatives of tetramethylene, Trans., 37.
Perkin, W. H., jun., and J. Stenhouse, the synthetical formation of closed carbon-chains. Part I (*cont.*): action of propylene bromide on the sodium compounds of ethyl acetoacetate and benzoylacetate, Trans., 68.
Perkin, W. H., jun. See also Brown, Mackenzie.
Perrier, G., metaphenyltoluene, 851.
Perrier. See Louise.
Perry, G. H. See Thorpe.
Pesci, L., mercuricanilido-compounds, 1448.
Pesci, L., so-called mercurous ammonium compounds, 685.
Petersen, E., allotropic state of some elements, 405.
Petersson, W., gadolinite, 1410.
Petit, P., distribution and condition of iron in barley, 1509.
—— product of the oxidation of starch, 1171.
—— production of dextrin, 577.
Petrenko-Kritschenko, P., derivatives of deoxybenzoïn, 1227.
Petrenko-Kritschenko, P. See also Melikoff.
Pfannenstill, E., xylenedisulphonic acids, 1340.
Pfeiffer, E., action of water on glass, 120.
Pfeiffer, H., partially miscible solutions, 1046.
Pflug, L. See Curtius.
Phookan, R. D., and F. Krafft, derivatives of sebacic acid, 1180.
Piccard, J., cantharene, 1480.
Piccini, A., new series of fluoroxy-compounds of molybdenum, 784.
Piccini, A., and G. Giorgis, fluoroxyvanadates, fluoroxyhypovanadates, and fluorovanadites, 785.
Pichard, P., comparative nitrification of humus and undecomposed organic matter, 906.
—— influence of the proportion of clay and organic nitrogen in fallow soils on the absorption of atmospheric nitrogen and the retention of nitrogen and nitrification, 656.
Pickering, S. U., chemical action at a distance, 269.
—— contraction on mixing sulphuric acid and water, 271.
—— cryoscopic behaviour of weak solutions, 678, 1045.
—— cryoscopy of cane sugar solutions, 109.
—— densities of sulphuric acid solutions, 272.
—— heat of dissolution of gases in liquids, 1042.
—— hypothetical manganese tetrachloride, 687.
—— strong solutions and the dissociation hypothesis, 108.
—— the densities of sulphuric acid solutions, 271.
—— the recognition of changes of curvature by means of a flexible lath, 767.
—— theory of residual chemical affinity as an explanation for the physical nature of solution, 559.
Pictet, A., and H. J. Ankersmit, phenanthridine, 196.

Pictet, A., and S. Erlich, methylphenanthridine and chrysidines, 197.
Pictet, A., and G. Krafft, chloriodides of organic bases, 1356.
Pictet, A., and S. Popovici, pyrogenic synthesis of isoquinoline, 730.
Pictet, R., physical and chemical phenomena at very low temperatures, 1138.
Picton, H., the physical constitution of some sulphide solutions, TRANS., 137.
Picton, H., and S. E. Linder, solution and pseudo-solution, TRANS., 148.
Picton, H. See also Linder.
Pieszczek, E., detection of tin, antimony, and arsenic, 918.
Pigeon, L., heat of formation of platinic bromide and its principal compounds, 3.
Piloty, O. See Fischer.
Pinette, J., estimation of fat in milk by Schmid's method, 1134.
—— soap analysis, 550.
Pinkus, G., action of trimethylene chlorobromide on some aromatic amines and amides, 1491.
Pinner, A., furfuran compounds, 1006.
—— mixed acid amides, 982.
—— nicotine, 1497.
—— so-called dibenzimidine, 1110.
Pinner, A., and R. Wolffenstein, nicotine, 1010.
Pinnow, J., action of benzenesulphonic chloride on amidoximes, 460.
Pionchon, J., specific heat and latent heat of fusion of aluminium, 1281.
Pirsson, L. V., gmelinite from Nova Scotia, 21.
Pirsson, L. V. See also Weed.
Pisani, F., cuprodescloizite from Mexico, 1055.
Plancher, G. See Mazzara.
Planck, M., recent developments of the mechanical theory of heat, 395.
—— theories of osmotic pressure and of electrolytic dissociation, 1143.
—— theory of diffusion and electrolysis, 935.
Plimpton, R. T., metallic derivatives of acetylene, PROC., **1892**, 109.
Plöchl, J. See Miller.
Plugge, P. C., reaction for cerous oxide, 239.
Pohl, J., aristolochin, 874.
Poliakoff, R. See Hell.
Polikier, H., synthesis of indole from tartaric acid and aniline, 66.
—— tartranilide, 54.
Pollak, A. See Goldschmidt.
Polonowsky, M. See Herzberg.
Pomeranz, C., bergaptene, the stearoptene of bergamot oil, 71.
Pope, W. J., the crystalline forms of the sodium salts of the substituted anilic acids, TRANS., 581.
Popoff, mechanism of the production of urea in the animal organism, 89.
Popovici, S. See Pictet.
Potilitzin, A., lithium bromate, 1275.
—— rate of decomposition of calcium chlorate by heat, 1275.
—— the hydrates of cobalt chloride and their alterations in colour, 571.
Poulenc, C., nickel and cobalt fluorides, 1159.
—— nickel potassium and cobalt potassium fluorides, 781.
Poulson, E., poisonous constituents of the ethereal extract of ferns, 380.
Pratesi, L., action of nitric acid on phenylglycollic acid, 607.
—— orthoparadinitrophenylglycollic acid, 1333.
—— supersaturated aqueous solution of carbonic anhydride, 1274.
Prausnitz, G., derivatives of 2-methyl-5-ethylpyridylalkine, 1358.
Prelinger, O., picric acid as a test for guanidine, 950.
Prendel, R., tourmaline from Siberia, 573.
Přibram, R. See Handl.
Přiwoznik, E., formation of sulphuric acid by burning illuminating gas, 1151.
—— formation of sulphuric acid and ammonium sulphate by burning coal gas, 1389.
Probst, O., derivatives of thiocarbamide and carbamide, 966.
Procter, H. R., analysis of gambier, 928.
Prud'homme, cuprammonium oxide, 18.
Prud'homme and C. Rabaut, conversion of aromatic amines into the chlorine derivatives of the hydrocarbons, 705.
Pullinger, W., platinum tetrachloride, TRANS., 422.
Pulvermacher, G., condensations with formaldehyde, 1450.
—— mandelamide, 1203.
—— reaction of trithioformaldehyde and formaldehyde, 579.
Pulvermacher, G., and W. Loeb, carbazole, 1466.
Pum, G., action of hydriodic acid on cinchonine, 514.
—— benzoyl derivatives of glucosamine, 134.

Purdie, T., and J. W. Walker, resolution of lactic acid into its optically active components, TRANS., 754.
Purfürst, C. See Ehrenberg.
Purgotti, A., new thiosulphates, 1418.
Puschl, C., expansion of water by heat, 1382.

Q.

Quenda, E., action of ethyl cyanacetate on aniline, 1072.
—— γ-substituted hydantoïns, 828.
Quincke, G., relations between compressibility and indices of refraction of liquids, 669.
Quincke, J., gasometric alkalimetry, and the employment of potassium ferricyanide in gasometry, 526.

R.

Raabe, F. F., assay of commercial toluidine, 925.
Rabaut, C., action of benzyl chloride on orthotoluidine, 48.
—— action of benzyl chloride on ortho- and para-toluidine, 313.
Rabaut, C. See also Prud'homme.
Rabinerson, J. See Michaelis.
Raczkowski. See De Raczkowski.
Rahnenführer, C. See Lossen.
Rammelsberg, C., hypophosphates, 403.
Ramsay, W., pedetic motion in relation to colloïdal solutions, PROC., **1892**, 17.
Ramsay, W., and H. Berghell, rock of the Jiwaara, in Finland, 1058.
Ransom, F., constituents of henbane seed, 231.
Raoult, F. M., determination of the freezing point of very dilute solutions: freezing points of dilute solutions of cane sugar, 678, 935.
Raps, G. See Claus.
Rassow, B. See Einhorn.
Raulin, J., influence of the nature of the soil on vegetation, 1121.
Rauter, G., silicon tetrachloride, 1273.
Rauter, G. See also Seubert.
Reboul, E., bromobutylenes, 127.
Recoura, A., chromosulphuric acid and metallic chromosulphates, 783.
—— green chromic sulphate, 411.
—— isomeric forms of chromic sulphate, 411.
Reformatsky, S., action of zinc and ethyl monochloracetate on the aldehydes, 1300.
Regelsberger, F., assay of aluminium and its alloys, 102, 535.
—— estimation of silicic acid in fluorides, 1128.
Reh, A. See Claus.
Reich, K., solubility of sodium carbonate and sodium hydrogen carbonate in solutions of sodium chloride, 116.
Reicher, L. T. See Van Deventer.
Reid, A. F., improvements in burettes, 1027.
Reid, E. W., absorption without osmosis, 646.
Reinhardt, C., estimation of phosphorus in pig-iron by means of Braun's centrifugal apparatus, 912.
Reis, M. A. v., estimation of manganese by the chlorate method, 1132.
Reissert, A., dyes obtained from ketomethyljuloline and methylepidone, 498.
—— julole, 496.
—— α-phenylhydrazidopropionic acid, 1456.
Reissert, A., and A. Junghahn, 3′-methyl-α-naphthindole, 1479.
Reissert, A. See also Kayser.
Remmler, W., separation of bismuth from lead, 385.
Remsen, I., double halogen salts, 779.
Rennie, E. H., and G. Goyder, the resins of *Ficus rubiginosa* and *F. macrophylla*, TRANS., 916.
Retgers, J. W., influence of foreign substances on the form, purity, and size of crystals separating from a solution, 937.
—— isomorphism, 1048.
Reuter, L., synthesis of cymene, 1310.
Reuter, L. See also Brühl, Krafft.
Reverdin, F., and C. de la Harpe, amidonaphtholsulphonic acids, 996.
Rey, H. See Lunge.
Reychler, A., constitution of carvene, 1350.
—— preparation of carvacrol, 1311.
—— some derivatives of carvacrol, 1312.
Reymond. See Du Bois Reymond.
Reynolds, J. E., silicon compounds and their derivatives. Part IV. The action of silicon tetrachloride on substituted phenylamines, TRANS., 453.
—— some silver compounds of thiourea, TRANS., 249.
Riban, J., alteration of chalybeate mineral waters, 1288.
—— basic zinc nitrate, 1156.
—— chalybeate mineral waters, 1289.
—— colorimetric estimation of iron, 1132.

Richards, J. W., specific heat of aluminium, 673.
Richards, T. W., cuprammonium acetobromide, 953.
Richardson, A., measurement of light intensity by the expansion of chlorine, 253.
Richardson, G. M., double halogen salts of tin, 784.
Richet, C. See Hanriot, Héricourt.
Richmond, H. D., estimation of iodoform, 1528.
Richmond, H. D., and H. Off, indications of a possible new element in an Egyptian mineral, Trans., 491.
Richter, E., β-trichloro-α-hydroxypropenylamidoxime, 321.
Riesenfeld, J. See Kühn.
Riggs, R. B., separation of iron, manganese, and calcium, 916.
Rimbach, E., behaviour of optically active substances in mixtures of two solvents, 1137.
Ringer, S., calcium salts and coagulation, 1112.
Rinne, F., gismondine from Westphalia, 1056.
—— relations between minerals of the heulandite and desmine groups, 417.
Riva-Rocci, S., estimation of peptones in stomach contents, 1136.
Rocci. See Riva-Rocci.
Rodewald, H., detection of margarin in butter, 1034.
Rodzyanko, A., some properties of humin and humic acid, 1372.
Röhmann, F., and W. Spitzer, determination of the affinity of organic acids by means of lacmoïd, 37.
Rössing, A. See Otto.
Rösing, E., oxidation of albumin in presence of sulphur, 741.
Röttger, H., assay of beeswax for vegetable wax, 551.
—— detection of resin in beeswax, 923.
Rohde, G. See Miller.
Romburgh. See Van Romburgh.
Roos, A. See Krafft.
Roos, E., diamines in disease, 518.
Roos, L., and E. Thomas, vegetation of the vine, 908.
Roozeboom, H. W. B., solubility curves of pairs of salts, 1384.
—— solubility of mixed crystals, especially of two isomorphous substances, 265.
—— solubility of mixed crystals of potassium and thallium chlorates, 266.
—— waters of the North Sea, 419.
Roscoe, H. E., and F. Scudder, note on the action of water gas on iron, Proc., **1891**, 126.
Rosenbusch, H. See Hunter.
Rosenstein, W. See Freund.
Rosenstiehl, A., influence of nucleal methyl on the properties of orthotoluidine, 1319.
Rossin, O., metahemipinic acid, 180.
Rossiter, E. C. See Armstrong.
Rothe, F. See Michaelis.
Rousseau, G., crystallised ferric oxychlorides, 119.
—— formation of saline hydrates at high temperatures, 119.
—— hydrated potassium manganites, 569.
Rousseau, G., and G. Tite, basic nitrates, 1157.
—— —— cadmium hydrosilicate, 1157.
—— —— decomposition of basic nitrates by water, 1272.
—— —— silver nitrosilicate: existence of a nitrosilicic acid, 684.
Rouvier, G., iodide of starch, 578, 801, 1171.
Roux, volumetric estimation of peptones in urine, 1264.
Rovighi, A., ethereal hydrogen sulphate in the urine, and the disinfection of the alimentary canal, 226.
Rubricius, H., estimation of manganese in iron and steel, 1030, 1524.
Rücker, A. W., density and composition of dilute sulphuric acid, 271.
Rüdel, C., alkaloïds of *Berberis aquifolium* and *B. vulgaris*, 641.
Rügheimer, L., condensation of aldehydes with benzoylpiperidine, 1364.
—— the compound $C_{36}H_{28}N_4O_6$ obtained by the action of sodium ethoxide on ethyl hippurate, 1002.
Rügheimer, L., and E. Mischel, diamidoacetone, 952.
Ruer, R. See Fittig.
Rürup, L., estimation of manganese in iron and steel, 916.
Ruhemann, A., paraxylalphthalide and its derivatives, 473.
Ruhemann, S., the isomeric α-bromocinnamic acids, Trans., 278.
Ruhemann, S., and R. S. Morrell, dicarboxyglutaconic acid, Trans., 791.
Ruhl, J., parathiophenylhydrazine and thionylthioaniline, 1326.
Ruhl, J. See also Michaelis.
Rumpf, estimation of phenols in human urine, 544.
Rung, F., and M. Behrend, glyoxaline, 1493.
Ruppert, F. See Fresenius.

Russanow, A., action of silver nitrite on methylene iodide, 1415.
—— phenylglyoximes, 321.
Rutishauser, R. See Kostanecki.

S.

Sabatier, P., and J. B. Senderens, action of nitric oxide on metallic oxides, 1151, 1271.
—— —— action of nitric oxide on metals, 1151.
—— —— action of nitric peroxide on metals and metallic oxides : nitrometals, 1390.
Sachs, H., thiophenchlorophosphine and its derivatives, 966.
Sachse, H. See Liebermann.
Saehsse, R., and A. Becker, kaolin in arable soils, 1026.
St. Martin. See De St. Martin.
Sakano, H. See Kellner.
Sakurai, J., determination of the temperature of steam arising from boiling salt solutions, Trans., 495.
—— modification of Beckmann's boiling point method of determining molecular weights of substances in solution, Trans., 986.
—— note on an observation of Gerlach of the boiling point of a solution of Glauber's salt, Proc., **1892**, 94.
Salkowski, E., influence of amidoacids on gastric digestion, 742.
Salvatori, S., derivatives of ethyl acetothienoneoxalate, 303.
Salzer, T., alkali citrates, 149.
—— iodometry, 1514.
—— water of crystallisation, 581.
Sandberger, F. v., minerals from the Fichtelgebirge, 1406.
Sanger, C. R., estimation of arsenic in wall paper, 382.
Sato, D. See Kellner.
Sauer, E., new drying apparatus for elementary analysis, 657.
Sauer, E. See also Weber.
Saunders, C. E., diazobenzene perbromide, 316.
—— double halogen salts of antimony, 788.
—— double halogen salts of manganese, 780.
Sautermeister, O., testing metallic iron for arsenic, 1030.
Saytzeff, A., stereoisomerism of oleïc and elaïdic acids, 812.
Schaap, Miss J., separation of salicylic acid from benzoic acid, 1532.
Schall, C., composition of ant oil, 948.
Schall, C., determination of vapour densities under diminished pressure, 553.
—— determination of vapour density, 934.
—— sodium phenyl sulphide, 970.
Schall, C., and C. Dralle, oxidation of brasilin : new derivatives of resorcinol, 502.
Schall, C., and S. Pasehkowetzky, stereoisomerides of carbodiphenylimide and carboparatolylimide, 1452.
Schall, C., and J. Uhl, action of iodoform on the additive product obtained from sulphurous anhydride and sodium phenoxide, 1076.
Scharfenberg, O. See Zincke.
Scheel, C., expansion of water, 7.
Scheibler, C., and H. Mittelmeier, so-called isoarabinic acid, 1180.
Scheidt, M. See Magnanini, Wislicenus.
Scherler, O., action of chlorine and of nitric acid on methylnaphthalenes, 593.
Scheurer-Kestner, action of carbon on sodium sulphate in presence of silica, 565.
—— decomposition of sulphurous anhydride by carbon at high temperatures, 681.
—— formulæ for calculating the heating power of coal, 1143.
Schierholz, C., separation of iodine, bromine, and chlorine, 1028.
Schiff, H., amidotolylurethane, 1203.
—— polymethylene bases from benzidine and tolidine, 1223.
Schiff, H., and A. Vanni, amidotolyloxamic and urethanotolyloxamic acids, 599, 1208.
Schiff, R., chloralimide, 134.
—— epiehloramine, 29.
—— special case of isomerism, 1067.
Schiff, R., and N. Tarugi, oximes of chloral and butylchloral, 33.
Schiffer, C. See Fittig.
Schiffer, H., derivatives of gallic acid and pyrogallol, 715.
Schiffer, H. See also Hautzsch.
Schimmel, constitution of betel oil, 833.
—— essential oils, 1347.
—— estimation of cinnamaldehyde, 924.
Schindler, T., erotonaldoxime, 32.
—— erotonaldoxime and allyl cyanide, 580.
Schjerning, H., estimation of calcium and magnesium in guncotton, 1520.
—— manganese compounds, 1052.
Schleicher, B., *a*-bromisovaleric acid : pimelic acid : synthesis of teraconic acid, 427.

Schlicht, A., estimation of oil of mustard, 1035.
Schliemann, J. See Lellmann.
Schlieper, F. W., reduction of metabromonitrophenol, 704.
Schlömann, W. See Schotten.
Schloesing, T., fermentation of farmyard manure, 1123.
Schloesing, T., jun., and E. Laurent, fixation of free nitrogen by plants, 378, 523, 1021.
Schmidt, A., and G. Wichmann, piperazine, 210.
Schmidt, A. See also Scubert.
Schmidt, C. See Witt.
Schmidt, E., action of hydriodic acid and of hydrobromic acid on neurine and choline, 808.
—— Berberis alkaloïds: berberine and hydroberberine, 1498.
—— choline, 219, 905.
—— choline, neurine, and allied compounds, 905.
—— hyoscine (scopolamine), 1255, 1498.
—— preparation of pure trimethylamine from crude trimethylamine hydrochloride, 805.
Schmidt, E., and A. Partheil, derivatives of allyltrimethylammonium hydroxide, 950.
Schmidt, E., and J. Weiss, allyltrimethylammonium chloride and iodide, 949.
Schmidt, G. C., critical temperatures of mixed liquids, 262.
—— vapour tension of homologous compounds, 396.
Schmidt, M., action of sulphurous anhydride on isonitroso-compounds, 476.
Schmidt, R. H., absorption and digestion of fat oils by plants, 1118.
Schmitt, physiological action of camphors and their combinations with chloral, 227.
Schmitter, new experiments on soil inoculation, 1512.
Schmitz-Dumont, W., insoluble sulphur, 1389.
Schmoeger, M., acetylated lactose and the optically different modifications of lactose, 948.
—— estimation of sugars by means of Ost's copper solution, 387.
Schneider, E. A., colloïdal silver, 117, 941.
—— organosols, 775.
—— preparation of pure colloïdal silver, 775.
Schneider, E. A., and F. W. Clarke, action of ammonium chloride at its dissociation temperature on silicates, 772.
Schneider, E. A. See also Clarke.
Schneider, R., reduction of potassium platinum thiostannate. Potassium thioplatinosate, 944.
—— two new seleno-salts, 281.
Schnelle, W., and B. Tollens, multirotation of rhamnose and of the saccharoses, 1420.
—— —— polarisation phenomena of galactonic acid and galactonolactone, 1432.
—— —— polarisation phenomena of gluconic acid and glucolactone, 1432.
—— —— polarisation phenomena of rhamnonic acid and rhamnolactone, 1431.
Schoder, R. See Baeyer.
Schönfeld, F. See Freund.
Schönflies, A., theories of the structure of crystals, 572.
Schöpff, M., acridone derivatives, 1223.
—— action of aniline on β-naphtholcarboxylic acid, 1476.
—— displacement of halogen atoms in the benzene ring, 335.
—— Friedel-Craft's synthesis, 337, 594.
Scholz, R., heat of dissolution of salts in water at 0°, 676.
Scholz, W. See Liebermann.
Schotten, C., and W. Schlömann, oxidation of piperidine and tetrahydroquinoline derivatives, 354.
Shottländer, P., metals of the cerium group, 686.
Schreinemakers, F. A. H., equilibrium of double salts of lead and potassium iodides with their aqueous solutions, 560.
Schubert, A., and Z. H. Skraup, action of hydriodic acid on quinine and quinidine, 640.
Schündelen, B. See Nietzki.
Schütt, F., determination of the molecular refraction of solid chemical compounds in solutions of the same, 929.
Schütte, W., alkaloids of the Solanaceæ, 231.
Schütze, M., colour and constitution of compounds, 561.
Schützenberger, P., compounds of carbon and silicon, 1050.
—— constitution of peptones, 1500.
—— nickel, 1158.
Schulthess, O. See Michael.
Schulz, O., action of quinone and its derivatives on the organism, &c., 1115.
—— apparatus for the estimation of carbonic anhydride in air, 533.

Schulze, C., and B. Tollens, disappearance of the multirotation of sugars in ammoniacal solution, 1419.
—— —— simple apparatus for evaporating under reduced pressure, 1386.
—— —— the pentosans of woody fibre, 1420.
—— —— xylose and its optical properties, 1420.
Schulze, E., β-galactan, 1171.
—— occurrence of guanidine in plants, 908.
—— test for guanidine, 926.
—— vegetable cell membranes, 907.
Schuster, F., action of benzaldehyde on 2 : 6-lutidine, 1360.
Schutt, F. T., analyses of apple tree leaves, 1372.
Schwicker, A., new reagent for acetone, 1032.
—— use of iodic and bromic acids in quantitative analysis, 1027.
Scudder, F. See Roscoe.
Seeberger, L. See Bamberger.
Seegen, J., sugar in blood, 743.
Seelig, E., derivatives of glycerol, 288.
Seibert, R. See Claus.
Seidel, P., fulminuric acid, 690.
—— fulminuric and deoxyfulminuric acids, 1417.
—— sulphonic acid obtained from 1 : 4-amidonaphthol, 721.
Seidmann, S. See Kostanecki.
Sell, W. J. See Easterfield.
Semmler, F. W., myristicin and its derivatives, 311.
Semmler, F. W., and F. Tiemann, oxygen compounds of ethereal oils, 868.
Senderens, J. B., action of sulphur on metallic solutions, 770.
Senderens, J. B. See also Sabatier.
Senger, O., absinthin from *Artemisia absinthium*, 1240.
Sénkowski, M., isomeric change in the synthesis of aromatic amines and phenols, 44.
Sestini, F., and R. Campani, detection of quinine and phenacetin in urine, 665.
Setschenow, J., analogies between solutions of a gas and of a salt, 397.
Seubert, K., and G. Rauter, copper oxalate and cuprammonium oxalate, 1431.
Seubert, K., and A. Schmidt, action of magnesium on chlorides, 776.
Seyewetz, A., action of phenylhydrazine on phenols, 49.
Seyler. See Hoppe-Seyler.
Shamel, C. H., eupatorin, 1103.
Sharpless, F. F. See Lane.
Shegog, T. A. See Adeney.
Shenstone, W. A., adhesion of mercury to glass in the presence of halogens, Trans., 452.
Shenstone, W. A., and C. R. Beck, platinous chloride and its use as a source of chlorine, Trans., 445.
Shields, J., conductivity of lead dioxide, 672.
—— occlusion of hydrogen by lead, 942.
Shinjo, S. See Kellner.
Shtchoukareff, A., degree of saturation of the dextroterpene from Russian turpentine, 1350.
—— reduction of hydrate of terpinol, 1351.
Siboni, G., condensation products of nitrobenzaldehydes with hydroxybenzenes, 621.
Siebert, C., lupanine, the alkaloïd of the blue lupin, 223.
Siegfeld, M., action of aniline on benzile, 1470.
Siegfeld, M. See also Auwers.
Sieker, F. A., and E. Kremers, menthene, 1479.
Sigalas, C. See Jolyet.
Sigmund, W., fat-decomposing ferments in plants, 1261.
Silber, P. See Ciamician.
Simonini, A., action of iodine on the silver salts of fatty acids, 1301.
Simon Thomas, J. C. A., attempted synthesis of a nitramine of the quinoline group, 725.
Sinclair, W. See Perkin.
Sisley, P. See Vignon.
Skinner, S., the physical properties of solutions of some metallic chlorides, Trans., 339.
Skraup, Z. H., compounds of the cinchona alkaloïds with hydriodic acid, 83.
Skraup, Z. H. See also Schubert.
Skubich, change of volume of solutions of salts, 766.
Smith, A. W., influence of substituting radicles on the configuration of aromatic ketoximes, 487.
Smith, C. G. See Gooch.
Smith, E. F., and R. H. Bradbury, estimation of molybdic and tungstic acids, 241.
Smith, E. F., and A. W. MacCauley, electrolytic separation of mercury from copper, 239.
Smith, E. F., and F. Muhr, electrolytic separation of iron, 917.
Smith, E. F., and D. L. Wallace, electrolytic separations, 920.

Smith, E. F., and D. L. Wallace, oxidation of copper glance by the electric current, 239.
Smith, J. H., new method for estimating organic nitrogen, 527.
Smith, J. L. See Haldane.
Smith, W. J., physiological action of sulphonal, 1507.
Smithells, A., note on the structure of luminous flames, TRANS., 217.
—— the origin of flame coloration, PROC., **1892**, 8.
Smithells, A., and H. Ingle, the structure and chemistry of flames, TRANS., 204.
Smyth, C. H., peridotite in Central New York, 1057.
Sobernheim, hæmatoporphyrinuria, 1118.
Sodeau, W. H., silver sulphite, 684.
Söderbaum, H. G., action of hydroxylamine on dibromopyruvic acid, 815.
Söderbaum, H. G. See also Abenius.
Soldaini, A., alkaloïds of *Lupinus albus*, 892.
Sonnenthal, S., dissociation in dilute solutions of tartrates, 588.
Sonnenthal, R. v., dissociation in dilute solutions of tartrates, 1144.
Soxhlet, sterilisation of milk, 518.
Soxhlet, V. H., indigo-green, 991.
—— preparation of flavin, 503.
Spehr, P., ephederine from *Ephedra monostachia*, 893.
Speyers, C. L., electromotive forces of metallic salts, 255.
Spica, M., behaviour of strontium tartrate with plastered wines, 93.
—— volumetric estimation of phosphoric acid, 912.
Spica, P., the mineral water of Monte di Malo, 1287.
Spica, P., and G. Carrara, thiazole compounds, 215.
Spiegel, L., action of phenylhydrazine on cantharidin, 999.
Spiegler, E., sensitive reaction for albumin in urine, 928.
Spilker, A. See Kraemer.
Spitzer, W. See Röhmann.
Spring, W., equilibrium of chemical systems under unequal pressures, 1148.
—— the formation of trithionate by the action of iodine in a mixture of sulphite and thiosulphate, PROC., **1892**, 91.
Spring, W., and E. Bourgeois, action of iodine on sodium hydrogen sulphite, 681.
Spring, W., and J. van Marsenille, thiopinacone, 1317.
Stackler, soluble naphthol compounds, 1116.
Stadt. See Van de Stadt.
Stahl, J., molybdic acid as a reagent for aromatic hydroxy-compounds, 1133.
Starling, E. H., and F. G. Hopkins, the urine in a case of phosphorus poisoning, 650.
Stavenhagen, A. See Claus.
Stelzner, R. See Marckwald, Moscheles.
Stenhouse, J. See Perkin.
Stern, J. See Fittig.
Stewart, A., thio-derivatives of orthamidobenzamide, 54.
Stewart, A. J. See Fischer.
Stewart, G. N., heat production in nerves during excitation, 365.
Stiassny, E., preparation of methylpropylacetic acid, 581.
Stich, respiration of plants under oxygen tension and when injured, 1259.
Stock, W. F. K., estimation of nitrogen in organic substances, 1516.
Stoehr, C., dimethyldiazine, 507.
—— pyridine and piperidine bases of the β-series, 628.
Stoehr, C., and M. Wagner, $\beta\beta$-dimethyldipyridyl, 629.
Stoehr, C. See Heuser.
Stohmann, F., and C. Kleber, hydrogenation of closed rings: constitution of camphoric acid, 1040.
Stohmann, F., and H. Langbein, calorific value of food constituents and their derivatives, 4.
—— —— thermochemistry of the carbohydrates and polybasic alcohols and phenols, 763.
Stokes, A. W., extraction of fat from milk solids, 391.
Stokes, G. G., optical proof of the existence of suspended matter in flames, 111.
—— the interactions occurring in flames, PROC., **1892**, 22.
Stolz, F., parethoxyphenylhydrazine and dimethylparethoxyphenylpyrazolone, 1080.
Stone, G. H., asphalt of Utah and Colorado, 21.
Stone, W. E., constituents of the nitrogen-free extract, 653.
—— digestibility of pentose-carbohydrates, 645.
—— estimation of pentoses in vegetables, 247.

Stortenbeker, W., compounds of chlorine with iodine, 1387.
Strache, H., estimation of aldehydic and ketonic oxygen, 546.
—— improvement in the method of estimating aldehydic and ketonic oxygen, 1530.
Straehe, H., and M. Kitt, oxidation of phenylhydrazine with Fehling's solution, 1322.
Strasser, L. See Bamberger.
Streintz, F., theory of secondary batteries, 1381.
Streintz, F. See also Neumann.
Ström, K. T. See Fittig.
Stutzer, A., analysis of healthy and diseased sugar cane, 1372.
—— composition of frozen and unfrozen beet chips, 1512.
—— digestibility of raw and boiled meat, 1367.
—— food value of brushwood. 1511.
Sudborough, J. J., isomeric change in the stilbene series, 1224.
Süllwald, A., estimation of nitrogen in pure and mixed nitrates, 528.
Sullivan. See O'Sullivan.
Swinburne, J., some points on electrolysis, 257.
Sykes, W. J., examination of vinegar, 251.
Szilasi, J., analyses of human milk, 517.
Szymanski, S. See Friedländer.

T.

Täuber, E., diphenyleneazone, 183, 482.
—— formation of an orthamidoditolylamine from parahydrazotoluene, 853.
—— synthesis of diamidocarbazole, 480.
Täuber, E., and E. Halberstadt, new synthesis of diphenylene oxide, 1470.
Tafel, J., acid hydrazides, 710.
—— colour reactions of acid anilides, 709.
—— oxidation of reduced pyridine and quinoline bases, 1104.
—— strychnine, 1012.
Tafel, J. See also Bölsing.
Tahara, Y., constitution of dehydrodiacetylpæonol and of dehydrodiacetylresacetophenone, 846.
—— orthohydroxyacetophenone, 844.
Tammann, G., measurement of osmotic pressure, 556.
—— metaphosphates, 1050.
—— Nasse's experiments on the excitability of frog-muscle in salt solutions, 515.
Tammann, G., permeability of precipitated membranes, 1383.
—— unorganised ferments, 899.
Tammann, G., and W. Nernst, maximum tension with which hydrogen is set free from solution by metals, 561.
Tanatar, S., action of alcoholic potash on bromisosuccinic acid, 1305.
—— action of methylene iodide on diethyl malonate, 1304.
—— complete transformation of fumaric into maleïc acid, 1306.
—— transformation of maleïc and fumaric acid, 1305.
Tarugi, N. See Schiff.
Tassinari, G., constitution of dihydroxythiobenzenes, 1316.
Tauf kirch, H. See Knorr.
Tavel, E., and A. Tschirch, iodine trichloride, 1388.
Tcherniac, J., estimation and preparation of thiocyanacetone, 1426.
—— monochloracetone, 1425.
—— thiocyanacetone, 1425.
—— water of crystallisation of barium thiocyanate, 1418.
Teclu, N., new laboratory burner, 768.
Terne, B., iron in bone-black, 1053.
Terreil, nickel and cobalt reactions, 1132.
Terreil, A., chromiferous clay from Brazil, 1057.
Thal, K., action of nitrous acid on ethyl acetosuccinate and diacetosuccinate, 1074.
Thiele, A., β-isopropylthiophen, 442.
Thiele, J., azodicarboxylic acid, 1429.
—— nitroguanidine and amidoguanidine, 1295.
Thiesing, H., methylenedibenzamide, 467.
Thörner, W., estimation of carbon in iron and steel, 913.
Thomas, E. See Berend, Roos.
Thomas. See Simon Thomas.
Thoms, H., constituents of the buds of *Chrysanthemum cinerariæfolium*, 349.
—— valuation of oil of cloves, 250.
Thomsen, J., thermochemistry of hydrazine and of hydroxylamine, 1143.
Thomson, R. T., and H. Ballantyne, revision of constants employed in the analysis of fat and oils, 547.
Thorpe, T. E., a lecture experiment to illustrate the phenomena of coal-dust explosions, Trans., 414.

Thorpe, T. E., and W. Kirman, fluorosulphonic acid, TRANS., 921.
Thorpe, T. E., and A. K. Miller, frangulin, TRANS., 1.
Thorpe, T. E., and G. H. Perry, interaction of iodine and potassium chlorate, TRANS., 925.
Thoulet, J., water from the Arctic Ocean, 1287.
Thurnlackh. See Garzarolli-Thurnlackh.
Tiemann, F., acetovannillone, 59.
—— action of benzenesulphonic chloride on amidoximes, 460.
—— action of nitrous acid on benzenylamidethoxime, 323.
—— amidoximes and azoximes, 135, 317.
—— constitution of the hydroxamic acids, 300, 461.
—— isoeugenol, diisoeugenol, and their derivatives, 45.
—— oxidation products of safrole, 46.
—— pæonolphenylhydrazone and oxime, 59.
—— phenyl-α-hydroxycrotonic acid, 471.
—— preparation of benzenylhydrazoximamidobenzylidine, 461.
—— reduction of aromatic aldehydes, 167.
—— vanilloylcarboxylic acid, 64.
Tiemann, F. See also Semmler.
Tilden, W. A., on limettin, TRANS., 344.
—— spontaneous conversion of isoprene into caoutchouc, 1482.
Tite, G. See Rousseau.
Tivoli, D. See Cavazzi, Pellizzari.
Tjelouchin, W., vivianite, 690.
Töhl, A., action of sulphuric acid on bromoprehnitene, 968.
—— action of sulphuric acid on chlorodurene, 968.
—— chlorodurenesulphonic acid, 1465.
—— halogen derivatives of methylbenzenes, 967.
Töhl, A., and A. Geyger, symmetrical and unsymmetrical ethylmetaxylene, 968.
Töhl, A., and D. v. Karchowski, ethylpseudocumene and the action of sulphuric acid on it, 990.
Töhl, A. See also Heise.
Tollens, B., reactions of xylose and arabinose, 290.
Tollens, B., and others, carbohydrates, 248.
Tollens, B., and P. Wigand, penterythritol, a tetrahydric alcohol, 127.
Tollens, B. See also Günther, Lindsey, Schnelle, Schulze.
Torup, S. See Bohr.
Traube, J., capillarity constants of salts at their melting points, 7.
—— cryoscopic behaviour of dilute solutions, 8.
—— cryoscopic communications, 765.
—— estimation of fusel oil in spirits, 543.
—— molecular volume of dissolved substances, 1383.
Traube, M., sulphuryl holoxide, 401.
Traube, W., amides and imides of sulphuric acid, 1389.
Trautmann, E. See Noelting.
Treadwell, F. P., estimation of sulphur, 1375.
—— milarite, 1056.
Treupel, G., carbohydrates of putrefying human urine, 226.
Trevor, J. E., mutual solubility of salts in water, 264.
Trillat, A., and De Raczkowski, azo- and alkyl-compounds of chrysaniline and the colouring matters derived therefrom, 1095.
Trimble, H., chestnut-wood tannin, 716.
Tscherven-Iwanoff, polymerides of dichloracetonitrile and trichloracetonitrile, 1291.
Tschirch, A. See Tavel.
Tubby, A. H., and T. D. Manning, human succus entericus, 1368.
Turner, C., preparation of orthonitraniline, 837.
Turner, T. See Barrows.
Tust, K., bromopianic acid, 1209.
Tuxen, C. F. A., rain as a source of nitrogen for vegetation, 233.
Twitchell, E., estimation of resin in its mixtures with fatty acids, 389.

U.

Uhl, J. See Schall.
Ulffers, F. See Bistrzycki.
Ullik, F., carbohydrates, 1066.
Ulrich, B. C., oxidation of bi-secondary pentethylphlorogluciuol by means of uncombined oxygen, 1188.
Ulsch, K., action of the copper-iron couple on nitrates and nitrites, 1518.
Umney, J. C. See Dunstan.
Urban, K. See Fittig.

V.

Van de Stadt, H. J. See Van Deventer.

Van Deventer, C. M., and L. T. Reicher, formation of salts in alcoholic solution, 262.
Van Deventer, C. M., and H. J. Van de Stadt, theory of the solubility curve, 559.
Van Dorp, W. A. See Hoogewerff.
Van Hise, C. R., iron ores of the Marquette district, Michigan, 794.
Van Leent, F. H. See Lobry de Bruyn.
Van Marsenille. See Spring.
Vanni, A. See Schiff.
Vanni, J., apparent variability of the electrical equivalent of copper, 105.
Van Nüys, T. C., and R. E. Lyons, carbonic anhydride in the urine, 649.
Van Romburgh, P., action of nitric acid on alkyl phenylcarbamates, 711.
—— action of nitric acid on dimethylorthanisidine, 159.
Van't Hoff, J. H., theory of solutions, 1045.
Varda. See De Varda.
Varet, R., action of ammonia on mercuric cyanide and its haloïd derivatives, 575.
—— action of metals on salts dissolved in organic liquids, 797.
—— piperidine compounds, 1483.
Vasey, S. A. See Heaton.
Vasileff, M. See Menschutkin.
Vaubel, W., phenylene oxide, 1187.
Veley, V. H., chemical changes between lead and nitric acid, 410.
Venable, F. P., preparation of pure zirconium chloride from zircons, 412.
Venturoli, G., estimation of hydrocyanic acid, 1530.
Verneuil, A., automatic return of mercury in Sprengel pumps, 8.
Vernon, H. M., manganese tetrachloride, 19.
—— maximum density of water, 7.
—— molecular weights of liquids as evinced by their boiling points, 107.
Vesterberg, A., hydrocarbons from α- and β-amyrin, 288.
—— oxidation products of the amyrins, 290.
Vèzes, M., chlorazopalladium compounds, 1284.
—— iodonitro- and bromonitro-platinum compounds, 280.
—— nitrogen compounds of platinum, 1283.
Vidal, R., action of non-metallic nitrides and hydronitrides on hydroxycarbon compounds, 1311.
Vignon, L., rotatory powers of various silks, 254, 645.
Vignon, L., specific gravity of silk, 1036.
Vignon, L., and P. Sisley, nitrated silk, 1111.
Villavecchia, V. See Nasini.
Ville, J., transformation in the animal economy of sulphanilic acid into sulphanilocarbamic acid, 903.
Vincent, C., and Delachanal, occurrence of mannitol and sorbitol in the cherry laurel, 908.
Viron, L., soluble colouring matters produced by bacteria in distilled medicinal waters, 907.
Vis, G. N., 1 : 4-ethoxyacetamidoquinoline, 1104.
Vitali, D., action of hydrogen cyanide on mercurous salts, 1416.
—— reactions of hydrastine and other alkaloïds, 755.
—— volumetric estimation of soluble sulphides, 1515.
—— volumetric estimation of the metals of the alkaline earths and of some heavy metals, 1521.
Vladesco. See Démètre-Vladesco.
Vogel, J. H., analysis of phosphates, 912.
—— estimation of lime in phosphates by Glaser's process, 534.
Vogt, J. H. L., composition of melilite, 1410.
Vogtherr, H., action of paramidodimethylaniline on ketones, 854.
Vogtherr, H. See also Jannasch.
Voit, C., J. G. Otto, A. C. Abbott, G. Lusk, and F. Voit, formation of glycogen from different sugars, 902.
Voit, F., behaviour of milk sugar in a diabetic, 903.
Volhard, J., compounds of thiophen and of its homologues, and of some ketones with mercuric chloride, 828.
—— hydrochelidonic acid or acetonediacetic acid, 432.
—— phenylhydrazonehydrazide of levulinic acid, 436.
—— preparation of maleïc anhydride, 963.
Volney, C. W., manufacture of nitric acid, 941.
Volpi, A., homologues of acridine, 342.
Voorhees, E. B., estimation of nitrogen, 751.
Voss, G. See Lossen.
Voswinkel, A., occurrence of gums which yield xylose, 380.
Vries. See De Vries.
Vulté, H. T. See Waller.

W.

Waage, T., presence and function of phloroglucinol in plants, 1120.
Wachter, W., desaurin, 1095.
Wachter, W. See also Meyer.
Wagner, G., oxidation of aromatic compounds containing the side chain C_3H_5, 310.
—— oxidation of mixed fatty ketones, 35.
—— oxidation of tertiary alcohols, 28.
Wagner, M. See Stoehr.
Walbaum, H. See Bertram.
Walden, P., affinity coefficients of organic acids and their relation to chemical constitution, 266.
Walker, J., preparation of alkyl iodides, Trans., 717.
—— the dissociation constants of organic acids, Trans., 696.
—— the methyl salts of camphoric acid, Trans., 1088.
—— the new theories of solution, 264.
Walker, J. W. See Purdie.
Wallace, D. L. See Smith.
Wallach, O., camphene and camphoric acid, 868, 1481.
—— camphor and fenchone series, 1236.
—— constitution of pinene, 997.
—— derivatives of carvole, 499.
—— isomerism in the limonene series, 1348.
—— menthylamine, 500.
Wallach, O., and A. Berkenheim, tetrahydropinene, 998.
Wallach, O., and E. Früstück, nitrolamines of pinene, 997.
—— —— preparation of pinole glycol and its derivatives, 998.
Wallach, O., and J. Griepenkerl, comparison of bornylamine and fenchylamine, 1238.
Wallach, O., and A. Hesse, action of chlorine on dihydrochloropentene, 1350.
Wallach, O., and L. Jenckel, fencholamine, 1240.
Wallach, O., and G. Lorentz, pinylamine, 996.
Waller, E., and H. T. Vulté, analysis of chromite, 1525.
Walter, G., oxidation of benzoyltetrahydroquinaldine, and nitro-derivatives of the same, 881.
Wanklyn, J. A., liquid and gaseous mixtures, 935.
Wanklyn, J. A., and W. Johnson, alde-acids, 696.
Wanklyn, J. A., and W. Johnstone, nature of solution, 108.
Wanklyn, J. A., W. Johnstone, and W. J. Cooper, change of volume on dissolution, 264.
Warden, C. J. H., ash of *Achryanthes aspera*, 230.
Warren, H. N., aluminium sulphide, 943.
—— electrolytic preparation of metallic alloys, 394.
—— new silver ore, 1404.
—— reducing action of graphitoïdal silicon, 115.
Warren, T. T. P. B., valuation of coal for use in steam boilers, 668.
Wasowicz, V. See Jannasch.
Weber, J., oil of cinnamon, 1509.
Weber, O., toluic sulphinide ("methylsaccharin"), 1092.
Weber, R., influence of the composition of the glass of slides and cover glasses on the durability of microscopic objects, 1276.
Weber, R., and E. Sauer, composition of glass suitable for chemical utensils, 410, 1052.
Wedemeyer, K. See Arnold.
Weed, W. H., a gold-bearing hot spring deposit, 24.
Weed, W. H., and L. V. Pirsson, sulphur, orpiment, and realgar in the Yellowstone Park, 283.
Wege, H., acetoximes, 333.
—— deoxybenzoïn, 338.
Wege, H. See also Meyer.
Wegscheider, R., methyl salts of abnormal structure, 1208.
Wehmer, C., absence of oxalates in young leaves as in the case of some phanerogamous parasites, 651.
—— formation and physiological significance of oxalic acid in fungi, 230.
Weil, A. See Claus.
Weinberg, A., paramidoalkylorthotoluidines 1078.
Weinschenck, E. See Kunz.
Weiske, H., influence of various salts on live weight and on the composition of bones and teeth, 647.
Weiss, J. See Schmidt.
Wells, H. L., and S. L. Penfield, salts of cæsium containing three atoms of halogen to one of metal, 773.
Wells, J. S. C., analysis of tin ores, 540.
—— separation of copper and cadmium, 534.
Welmans, P., detection of vegetable oils in lard, 1133.
Werigo, B., influence of oxygen in

the separation of carbonic anhydride in the lungs, 1369.
Werigo, B., presence of pentamethylenediamine in pancreatic extracts, 1368.
Werner, A., basic calcium nitrate, 1276.
—— stereoisomeric derivatives of benzhydroxamic acid, 461.
Werner, E. A., chemistry of the thioureas, Part II, Proc., 1892, 96.
Westberg, A., toxic action and detection of carbon bisulphide, 1520.
Wheeler, H. A. See Luedeking.
Wheeler, H. L. See Comstock.
White, J. See Morse.
White, W. H., treatment of chlorosis by hydrochloric acid, 1117.
Whitehead, C., estimation of small quantities of silver and gold in base metals, mattes, &c., 1525.
—— use of cadmium in assaying gold, 919.
Whiteley, R. L., and J. T. Wood, Lowenthal's method of tannin analysis, 667.
Wichelhaus, H., methylnaphthalenes, 492.
Wichmann, G. See Schmidt.
Widman, O., intramolecular change of the propyl group, 43.
—— nomenclature of compounds containing nitrogenous nuclei, 875.
—— thaumasite, wollastonite, chabasite, and vesuvian, 1407.
Wiechmann, F. G., estimation of mixtures of saccharose, fruit sugar, and dextrose or levulose, 248.
Wiesner, J., examination of different forms of carbon, 1273.
Wigand, P. See Tollens.
Wiklund, C. L., phosphoric acid in soil, and its estimation, 750.
Wildermann, M., exchange of chlorine, bromine, and iodine between inorganic and organic haloïd compounds, 574.
—— method for determining the constitution of saturated and unsaturated halogen derivatives and hydrocarbons, 285.
Wildermann, M., and S. Aisinmann, velocity of the reaction between alcoholic potash and alkyl halides, 399.
Will, W., osazone of hydroxypyruvic acid, 356.
Willard, J. T., and G. H. Failyer, extraction apparatus, 910.
Willgerodt, C., constitution of nitroso-azo-compounds, 1321, 1453.
—— dinitrosoazobenzene, 1079.
Willgerodt, C., first reduction products of the nitro-group, 594.
—— metadinitrobenzene, 704.
Willgerodt, C., and E. G. Mühe, derivatives of phenylhydrazine, 453.
William. See Mac William.
Williams, J. F. See Bracket.
Williams, G. H., crystals of metallic cadmium, 1398.
Williams, Miss K. J., the composition of cooked vegetables, Trans., 226.
Wilm, T., lecture experiment, 563.
—— palladious oxide, 572.
Wilson, J. A., action of alkaline mercuric cyanide on maltose, dextrose, and dextrin, 1032.
Wilson, J. A., estimation of combined alkali in soap, 384.
—— separation of resin from fatty acids, 546.
Wilson, J. M., standardising iodine solutions for the estimation of sulphur in steel, &c., 382.
Winkler, L. W., absorption of gases by liquids, 556.
—— solubility of gases in water, 271.
Winternitz, H., colour reactions of the proteïd precipitate produced by potassium ferrocyanide, 1036.
—— putrefaction of milk, 1116.
Winterstein, E., vegetable amyloïd, 803.
Wislicenus, W., inactive ethyl malate, 1431.
—— β-methylmalic acid, 589, 963.
—— reduction of ethyl oxalacetate, 147.
—— synthesis of hydrogen nitride, 1151.
Wislicenus, W., and M. Scheidt, action of phenylhydrazine on ethyl ethoxyoxalacetate, 458.
—— —— combination of phenylhydrazine with ethyl oxalacetate, 49.
Witt, O., derivatives of paranitrorthochlorobenzyl bromide, 444.
Witt, O. N., β-naphthaquinonesulphonic acids, 196.
—— sulphonic acids of amido-α-naphthol and α-naphthaquinone, 722.
Witt, O. N., and H. Kaufmann, α-naphthol-α-sulphonic acid, 194.
Witt, O. N., and C. Schmidt, azonium bases, 1246.
—— —— products of the reduction of alkylated azo-colours of the naphthalene series, 862.
Witter, H. See Buchner.
Wolf, H. See Freund.
Wolf, J., estimation of calcium salts in syrup and sugar products, 1377.

Wolffenstein, R., oxidation of piperidine with hydrogen peroxide, 1484.
Wolffenstein, R. See also Pinner.
Wood, J. T. See Whiteley.
Wreszinski, H. See Fischer.
Wright, A. E., plasma and serum, 1113.
—— tissue fibrinogens, 646.
Wülfing, E. A., the pyroxene family, 1408.
Wüllner, A. See Koch.
Wynne, W. P., action of sulphuryl chloride on acetorthotoluidide and acetoparatoluidide: mono-, di-, and tri-chlorotoluenesulphonic acids, TRANS., 1042.
—— note on the constitution of Nevile and Winther's orthotoluidinesulphonic acid, and of the sulphonic acids of orthochloro- and orthobromotoluene, TRANS., 1036.

Y.

Young, condensation of the three isomeric methylhydrocinnamic acids to the corresponding methylhydrindones, 1221.
Young, R. A., retiform tissue, 1113.
Young, W. C., volatile organic matter in potable water: method of estimating dissolved, fixed, and volatile organic matter in water, 921.

Z.

Zaloziecki, R., Glauber's salt in the potash mines of Kalusz, 1286.
—— pyridine-like bases in petroleum, 1357.
Zanetti, C. U., constitution of the ethylpyrrolines, 350.
—— determination of the constitution of the homologues of pyrroline, 74.
Zanetti, C. U. See also Ciamician.
Zanoli, E. See Goldschmidt.
Zatti, C., and A. Ferratini, action of methyl iodide on α-methylindole, 614.
—— —— molecular weight of nitrosoindole, 67.
Zelinsky, N., stereoisomeric dimethyladipic acids and dimethylpimelic acids, 430.
—— stereoisomerism of dimethyldihydroxyglutaric acid, 436.
Zelinsky, N., and A. Buitchichin, an additive compound of hydrogen cyanide with ethyl α-cyanopropionate, 1301.
Zemjatschensky, P. A., iron ores of Central Russia, 689.
Zenoni, M. See Bertoni.
Zincke, T., action of bleaching powder and of hypochlorous acid on quinones, 720, 859, 970.
—— action of chlorine on phenols, 1186.
—— nitro-β-naphthaquinone, 1229.
Zincke, T., and T. Arnst, tetrachlororthodiketohydronaphthalene, its hydrates and alcoholates, 858.
Zincke, T., and O. Fuchs, hexachlorometadiketohexenes, 1461.
—— —— hexachloroparadiketohexene, 447.
Zincke, T., and M. Latten, action of chlorine on nitro-β-naphthaquinone in glacial acetic acid solution, 1229.
Zincke, T., and O. Scharfenberg, action of chlorine on nitro-β-naphthaquinone in chloroform solution, 1232.
Zink, J. See Amthor.
Zinkeisen, H., manganese spar and celestine from Scharfenberg, 1406.
Zinsser, F. J., aromatic nitriles, 344.
Zuco. See Marino-Zuco.
Zufall, A. See Lange.
Zunc, detection of resin oil in terebenthene, 923.

INDEX OF SUBJECTS.

ABSTRACTS. 1892.

And also to Transactions, 1892 (marked TRANS.); and to such papers as appeared in the Proceedings during the Session 1891—1892 (Nos. 101 to 114; Nov., 1891, to July, 1892), but not in Transactions (marked PROC.).

A.

Absinthin, from *Artemisia absinthum*, 1240.
Absorbent power of coloured salts and electrolytic dissociation, 757.
Absorption and digestion of fat oils by plants, 1118.
—— coefficients of gases, 1043.
—— of gases by liquids, 556.
—— spectra of thin metallic films, 1037.
—— without osmosis, 646.
Acenaphthalide, ortho- and para-nitro-*α*-, action of bromine on a mixture of, PROC., **1891**, 186.
Acenaphthene, oxidation of, 863.
Acenaphthenequinone, 864.
Acetal, amido-, preparation of, 1327.
Acetaldehyde, action of zinc and ethyl chloracetate on, 1300.
—— condensation of, with aniline, 1191.
Acetaldehydeaniline, 1191.
Acetaldoxime, 951.
—— action of hydrocyanic acid on, 1196.
—— preparation of, TRANS., 473.
Acetaldoximes, existence of two crystalline, TRANS., 470; PROC., **1892**, 135.
Acetalylcarbamide, 1327.
Acetalylmetaxylylthiocarbamide, 1329.
Acetalyl-*α*-naphthylthiocarbamide, 1331.
Acetalylparatolylthiocarbamide, 1328.
Acetamide, brom-, 827.
Acetamidine nitrite, 53.
—— picrate, 705.
Acetamidobenzylacetanilide, ortho-, 81.
Acetamidocarbazole, 616.
Acetamidonitrosocarbazole, 616.
Acetamidophenylsulphonepropionic acid and its halogen derivatives, 1090.
Acetamidotolyloxamethane, 599.
Acetamidotolylurethane, 1203.
Acetanhydrocitric acid, TRANS., 1003.
—— —— action of aniline on, TRANS., 1006.
—— —— conversion of, into aconitic acid, TRANS., 1007.
Acetanilide, nitrodibromo-, 1205.
Acetanilidobutyric acid, 1338.
Acetanilidoisobutyric acid, *β*-, 1339.
—— lactone, 1339.
Acetenyltrimethylammonium hydroxide, 905.
—— salts, 807.
Acetic acid, heats of combustion and formation of, 1139.
—— —— oximido-, 699.
—— —— production of, from cellulose, 1421.
—— fluoride, 1068, 1069.
—— sulphide, 300, 581.
Acetimido-*β*-chlorethyl ether, 1332.
Acetoacetanilide, 708.
Acetoacetic acid, phenylhydrazine salt of the hydrazone of, 162.
Acetoacrylic acid, diiodo-, 1179.
—— —— perchloro-*β*-, 1186.
—— oxime, 1179.
—— —— iodo-, 1179.
Acetocitric acid, TRANS., 1005.
—— —— reduction of, TRANS., 1009.
Acetodiketohexamethylenedicarboxylic acid, 586.
Acetoisobutyl alcohol, TRANS., 71.
—— bromide, TRANS., 72.
Acetoisobutyric acid, *β*-, derivatives of, 74.

Acetol ethyl ether, 954.
Acetomesitylene, action of hydroxylamine hydrochloride on, 314.
Acetonaphthalide, α-, physiological action of, 366.
Acetonaphthalide, β-, 4:1-bromiodo-, TRANS., 767.
—— 1:4-chlorobromo-, TRANS., 768.
Acetone, chlor-, 1425.
—— detection of, 1032.
—— diamido-, 952.
—— hydrazone, TRANS., 787.
—— symmetrical dichloro-, preparation of, 952.
—— thiocyan-, 1425, 1426.
Acetonediacetic acid, 432.
Acetonedicarboxylic acid, action of diazobenzene on, 161.
—— —— action of phenylhydrazine on, 162.
—— —— reduction of, 147.
Acetonedisazobenzene, 710.
Acetoneresorcinol, 1312.
Acetonitrile, di- and tri-chloro-, polymerides of, 1291.
Acetophenone mercuric chloride, 829.
—— sodium derivative of, 170.
Acetophenonethiophenylhydrazone, 1326.
Acetopiperone, 873.
Acetoprotocatechone, 61.
Acetothienone mercuric chloride, 829.
Acetothienoneoxalic acid, 154.
—— —— oxime of, 304.
Acetothiosulphuric acid, salts of, 1419.
Acetotoluidide, meta-, parabromo-, 1201.
—— —— parachloro-, 1201.
Acetotoluidide, ortho-, action of sulphuryl chloride on, TRANS., 1042.
—— —— derivatives of, 838.
—— —— nitrobromo-, 1207.
Acetotoluidide, para-, action of sulphuryl chloride on, TRANS., 1042.
—— —— 2:6-dibromo-, 175.
—— —— metachloro-, 450.
—— —— 6:3-nitrochloro-, 173.
Acetovanillone, 59.
—— derivatives of, 61.
—— synthesis of, from guaiacol and acetic acid, 61.
Acetovanillonephenylhydrazine, 61.
Acetoveratrone, 61.
Acetoxime, action of diazobenzene on, 1080.
—— action of hydrocyanic acid on, 1196.
Acetoxime-β-naphthylsulphone, 334.
Acetoximeparatolylsulphone, 334.
Acetoximephenylsulphone, 334.
Acetoximes, 333.
—— physiological action of, 1506.
Acetoxydichloropyridone, 449.
Aceto-xylide, parachlorometa-, 1202.
Acetoxytetramethylenecarboxylic acid, TRANS., 45.
Acetyl, magnetic rotation of substances supposed to contain, TRANS., 800.
Acetyl-α-acetaldoxime, PROC., 1892, 136.
Acetylacetone, magnetic rotation of, TRANS., 813, 840, 844.
—— refractive and dispersive powers of, TRANS., 846.
Acetylacrylic acid, dibromo-, 302.
—— —— trichloro-, action of hydroxylamine on, 1203.
Acetylamidoguanidine salts, 1297.
Acetylamidoisophthalic acid, 1464.
Acetylbenzamide, 982.
Acetylbenzeneazoacetone, 977.
Acetylbenzenehydrazo-orthocresol, 975.
Acetylbenzoylmethyl cyanide, 451.
Acetylbenzylmetaxylidine, 1320.
Acetylbenzylorthotoluidine, 48.
Acetylbutylchloraldoxime, 34.
Acetylcamphorylphenylhydrazine, 1481.
Acetylchlorantiglyoxime, 694.
Acetylchlorophenols, isomeric, 308.
Acetyldinitrocarvacrol, 309.
Acetyldiorthotolylhydrazine, 843.
Acetyldiparatolylhydrazine, 844.
Acetyldiphenylhydrazine, 710, 843.
Acetylene, formation of, from bromoform, 421.
—— formation of, in the interior of a luminous flame, TRANS., 325.
—— higher homologues of, 1163.
—— metallic derivatives of, PROC., 1892, 109.
—— origin of, in flames, PROC., 1892, 47.
—— silver and copper compounds of, 1416.
Acetylenedicarboxylic acid, diiodo-, 431.
Acetylenic hydrocarbons, action of organic acids on, 1064.
Acetyl-β-ethylthiophen, 830.
Acetylfenchylamine, 1239.
Acetylfluorescin, 1319.
Acetylglycerol, dichloro-, 289.
Acetylguvacine, 740.
Acetylhydrindigotin, 480.
Acetylhydroximidoacetonitrile, 816.
Acetylindigotin, 480.
Acetylisoeugenol, 46.
Acetylmetachlorobenzeneazoparacresol, 975.
Acetylmetachlorobenzenehydrazoparacresol, 975.
Acetylmethylphenyltetrahydroquinazoline, 81.

Acetyl-β-methylthiophen, 830.
—— bromo-, 830.
Acetylmethyltrimethylenecarboxylic acid, oxime of, TRANS., 70.
—— —— preparation of, TRANS., 69.
Acetyl-β-naphthylglycocine, 1342.
Acetyl-α-naphthylhydrazine, 509.
Acetyl-α-naphthylthiocarbizine, 510.
Acetylnicotenylamidoxime, 207.
Acetylorthohomoparahydroxybenzonitrile, 320.
Acetylorthotolylglycocine, 1334.
Acetylorthotolylhydrazine, 843.
Acetylortho-xylene, 1 : 2 : 4-, production of, from camphor, PROC., **1892**, 54.
Acetylpæonol, 59. 845.
Acetylparabromodiphenylhydrazine, 982.
Acetylparabromophenylhydrazine, 982.
Acetylparachlorobenzeneazoparacresol, 974.
Acetylparachlorobenzenehydrazoparacresol, 974.
Acetylparachlorothiophenol, 308.
Acetylparethoxyphenylhydrazine, 1081.
Acetylparahomosalicenylamidoxime, 319.
Acetylparahomosalicylonitrile, 318.
Acetylparatolueneazoparacresol 974.
Acetylparatolylglycocine toluidide, chlor-, 1336.
Acetylparatolylhydrazine, 844.
Acetylphenoldisazotoluene, 976.
Acetylphenoxyethane, *aa'*-, 811.
Acetylphenylhydrazine, chlor-, 844.
Acetylphenylmethylhydroisopyrazolone, 635.
Acetylpropionyl, preparation of, 426.
Acetylquinaldine, para-, 1488.
Acetyltetrachlorocrotonic acid, dichloro-, 1462.
—— —— trichloro-, 1463.
Acetylthiocarbimide and aldehyde-ammonia, TRANS., 530.
Acetylvanillonitrile, 318.
Acherontia atropos, blood of, 648.
Acid amides, mixed, 982.
Acids, affinity coefficients of, 1269.
—— amido-, action of hydriodic acid on, 38.
—— and bases, study of the chemical neutralisation of, by means of their electrical conductivities, 2.
—— astringent, estimation of, in wine, 246.
—— bibasic organic, thermochemistry of, 395, 1140.
—— fatty, action of iodine on the silver salts of, 1301.
—— —— action of, on olefines, 1162.
—— —— dry distillation of silver salts of, 37, 293, 811.
Acids, fatty, estimation of resin in admixture with, 389, 546.
—— —— higher, action of bromine on, 695.
—— —— polybasic, synthesis of, 41.
—— free, estimation of, 539.
—— —— in spirits, estimation of, 387.
—— influence of, on the velocity of the hydrolytic action of yeast, TRANS., 940.
—— isodynamic, PROC., **1892**, 103.
—— ketonic, behaviour of, towards sodium hydrogen sulphite, 148.
—— mechanical determination of the boiling points of, 1039.
—— monobasic, existence of acid or basic salts of, in very dilute solution, 110.
—— polybasic, electrolytic conductivity of, 1145.
—— of butter, 1113.
—— organic, affinity-coefficients of, and their relation to chemical constitution, 266.
—— —— determination of the affinity of, 37.
—— —— dissociation constants of, TRANS., 696.
—— —— influence of boric acid on the electrical conductivity of aqueous solutions of, 257, 1265.
—— standard, use of potassium hydrogen tartrate for titrating, 525.
—— unsaturated, 812, 956.
—— —— conversion of, into their stereochemical isomerides by soda, 297.
—— —— decomposition of the dibromides of, by warm water and dilute alkalis, 959.
—— —— oxidation of, 956.
—— velocity of reaction in mixtures of isohydric and non-isohydric solutions of, 936.
Acidyl sulphides, 300, 581.
Aconine, TRANS., 393.
—— action of methyl iodide on, TRANS., 403.
—— conversion of, into aconitine, TRANS., 401.
—— crystalline salts of, TRANS., 399.
—— decomposition products of, TRANS., 402.
—— distillation of, with baryta, 1255.
—— hydrochloride, crystalline, preparation of, TRANS., 397.
—— properties of, TRANS., 400.
Aconite, alkaloids of, TRANS., 385, 395.
—— preparations, assay of, 392.
Aconitic acid, anhydro-derivatives of, TRANS., 1003.

Aconitic acid, conversion of acetanhydrocitric acid into, TRANS., 1007.
—— —— dissociation constant of, TRANS., 707.
—— anhydride, TRANS., 1009.
—— —— action of ammonia on, TRANS., 1010.
Aconitine, 1254, TRANS., 390.
—— conversion of aconine into, TRANS., 401.
—— hydrolysis of, TRANS., 396.
—— methiodide, TRANS., 403.
—— methohydroxide, TRANS., 404.
—— reaction for, 756.
Aconitum napellus, alkaloïds of true, TRANS., 385.
Acridine, homologues of, 342.
Acridinemethylium hydroxide, 881.
Acridine-series, action of alkalis on the alkyl iodides of, 879.
Acridone, 1086.
—— derivatives of, 1223.
Acridonesulphonic acid, 3-, 1223.
Acrylic acid, diiodo-, 431.
Action at a distance, 956, 1149.
—— —— —— of aqueous solutions on water vapour, 936.
Adenine, 219, 220, 890.
—— bromination of, 221, 890.
—— bromo-, 890.
Affinity coefficients of acids, 1269.
—— —— of alkyl bromides and iodides, 1289.
—— —— of organic acids and their relation to chemical constitution, 266.
—— of organic acids, determination of, 37.
—— residual chemical, theory of, as an explanation of the physical nature of solutions, 559.
Agrostemma githago, sapotoxin from, 350.
Air vitiated by respiration, 1502.
Albumin, ash free, 645.
—— decomposition of, 515.
—— detection of, in urine, 667, 928.
—— egg, crystalline, 515.
—— formation of furfuraldehyde from, 1433.
—— new, from protoplasm, 86.
—— oxidation of, in presence of sulphur, 741.
Albumins, transformations of, 362.
Albumone, 225.
Albumoses, salicylsulphonic acid as a test for, 552.
Alcohol, detection of higher alcohols in, 1379.
—— estimation of, 1529.
—— is, eliminated by the milk? 365.
—— indirect estimation of, 543.
Alcohol, oxidation of, by permanganate, 1529.
—— Röse's process for the estimation of, 1031.
—— solutions, dilute, cryoscopy of, 1045.
Alcoholic fermentation, influence of oxygen and concentration on, TRANS., 369.
—— function, primary, value of the, 799.
—— —— tertiary, value of, 1066.
Alcohols, higher, detection of, in spirits of wine, 1379.
—— —— in spirits, estimation of, 387.
—— mechanical determination of the boiling points of, 1039.
—— polybasic, thermochemistry of, 763.
—— primary, direct synthesis of, 27.
—— tertiary, oxidation of, 28.
Aldeacids, 696.
Aldehyde. See Acetaldehyde.
Aldehyde, tetracarbon, presence of, in brandy, 810.
Aldehyde-ammonias, compounds of thiourea and thiocarbimides with, TRANS., 509.
Aldehydes, action of sodium on, 169.
—— action of zinc and ethyl chloracetate on, 1300.
—— aromatic, reduction of, 167.
—— bromo-, formation of, by the action of bromine on alcohols of the ethyl series, 809.
—— colour reaction of, with aromatic nitro-compounds, 1263.
—— condensation of, with azo-compounds, 854.
—— condensation of, with benzoylpiperidine, 1364.
—— fatty, condensation of, with dicyanophenylhydrazine, 596.
—— occurrence of acetyl derivatives in the urine of animals after ingestion of, 1504.
—— sodium nitroprusside as a reagent for, 924.
Aldehydic oxygen, estimation of, 546. 1530.
Aldol, preparation of, 1423.
Aldoximeacetic acids, configuration of, 1069.
Aldoximes, action of acetic anhydride on, 1174.
—— configuration of, 1174.
—— conversion of, into nitriles, 1174.
—— molecular transformations of, 163.
Alimentary canal, absorption of water from, 1258.
—— —— disinfection of the, 226.
Alizarinamide, β-, preparation of, 864.

Alkali carbonate, normal, detection of, in hydrogen alkali carbonate, 1130.
—— combined, in soap, estimation of, 384.
—— hydroxides, estimation of, 526.
Alkaline earth metals, direct combination of nitrogen with, 566.
Alkaline earths, action of sulphur and water on, 770.
—— —— characteristics of, 17.
Alkalis, action of sulphur on, 770.
—— influence of, on the hydrolytic action of yeast, Trans., 936.
—— standard, use of potassium hydrogen tartrate for titrating, 525.
Alkaloïd from chrysanthemum flowers, 84.
—— from *Corydalis tuberosa*, Trans., 244, 605.
—— from Javan coca leaves, 361.
Alkaloïds, free, estimation of, and of their molecular weights, 666.
—— influence of, on the germination of seeds, 228.
—— of *Belladonna*, 1498.
—— of *Berberis*, 641, 1498.
—— of *Berberis aquifolium* and *B. vulgaris*, 641.
—— of *Lupinus albus*, 892.
—— of the Areca nut, 737.
—— of the root of *Corydalis cava*, 1366.
—— of the Solanaceæ, 213.
—— of true *Aconitum napellus*, Trans., 385.
—— reactions of, with potassium platinothiocyanates, 287.
Alkyl and acidyl sulphides, 300, 581.
—— bromides and iodides, affinity coefficients of, 1289.
—— halides and alcoholic potash, velocity of reaction between, 399.
—— —— halogenation of, 577, 1414.
—— iodides, preparation of, Trans., 717.
—— phenylcarbamates, action of nitric acid on, 711.
Alkylacetonedicarboxylic acids, 148.
Alkylcamphors, preparation of, 72.
Alkylcyanocamphors, 1344.
Alkylorthotoluidines, paramido-, 1078.
Allanite from Gyttorp, Sweden, 1409.
Allocinnamic acid, condensation of, with phenols, 848.
—— —— formation of, from phenylpropiolic acid, 848.
Allotropic states of some elements, 405.
Alloxanhydrazone, 442.
Alloys, change of voltaic energy of, during fusion, 254.
—— estimation of gold, tin, and cadmium in, 1030.
Alloys, metallic, electrolytic preparation of, 394.
—— micrographic analysis of, 1399.
Allyl cyanide, constitution of, 27.
—— fluoride, action of halogens on, 800.
—— phenylamidoacetate, 468.
—— sodionitro-, 1062.
—— sodium thiosulphate, 1418.
Allylacetic acid, oxidation of, 958.
Allylcarbaminesodiocyamide, 703.
Allyldithiobiuret, α-, 704.
Allylethylsuccinic acids, 697.
Allylformamidine bisulphide, 292.
Allylfurfurylthiocarbamide, 43.
Allylisobutylthiocarbamide, symmetrical, 702.
Allylmethylsuccinic acids, 697.
Allylmelhylthiohydantoïn, 151.
Allylnitrolic acid, 1063.
Allylthiocarbamide, action of bromine on, Trans., 545.
Allylthiohydantoïn, 151.
Allyltrimethylammonium hydroxide, 905.
—— —— derivatives of, 950.
—— salts, 949.
Alum, detection of, in wines, 1522.
Alumina, volumetric estimation of, 535.
Aluminium, action of certain liquids on, 687, 1281.
—— action of chlorine and of bromine on, 118.
—— action of mercuric cyanide dissolved in water and in organic solvents on, 797.
—— action of nitric acid on, 1403.
—— analysis of, 1130.
—— and iron, estimation of, by the Glaser method, 755.
—— —— estimation of, in the presence of phosphoric acid, 755.
—— and its alloys, assay of, 535.
—— commercial, assay of, 102, 535.
—— condition of, in cast iron, 19.
—— direct estimation of, in iron and steel, 102.
—— estimation of, in phosphates, 536.
—— hydroxide, colloïdal solution of, Trans., 154.
—— in mineral waters, 1287.
—— occlusion of hydrogen by, 567.
—— phosphate, action of ammonium citrate on, 1127.
—— —— estimation of, 1522.
—— potassium fluoride, 1162.
—— specific heat of, 673.
—— —— —— and latent heat of fusion of, 1281.
—— suitability of, for domestic purposes, 687. 1281,
—— sulphide, 943.

Amalgams, electrolytic estimation of metals as, 753.
Amanita pantherina, toxic principle of, 232.
Amber, so-called, of Cedar Lake, Canada, 573.
Amethylcamphophenolsulphone, action of nitric acid on, 999.
Amethylcamphophenolsulphonic acid, action of nitric acid on, 999.
Amides, aromatic, action of trimethylene chlorobromide on, 1491.
—— dehydration of, in contact with diphenyl-derivatives, 617.
Amidines, 51.
—— action of nitric acid on, 951.
Amido-acids, action of hydriodic acid on, 38.
—— influence of, on gastric digestion, 742.
Amidoazobenzene, action of aniline hydrochloride on, 492.
Amido-groups in organic bases, method of determining the number of, PROC., **1892**, 133.
Amidosulphonic acid, 700.
Amidoximes, 135, 317.
—— action of benzenesulphonic chloride on, 460.
Amines, aromatic, action of trimethylene chlorobromide on, 1491.
—— —— conversion of, into chlorine derivatives of the hydrocarbons, 705.
—— —— isomeric change in the synthesis of, 44.
—— fatty, unsaturated, 30, 578.
—— primary, preparation of, by means of potassium phthalimide, 157.
—— tertiary aromatic, action of arsenic chloride on, 1321.
Ammonia, action of magnesium on, 409.
—— alcoholic solutions of, 1049.
—— excretion of, 365.
—— in the atmosphere and rain water of the tropics, 381, 909.
—— reduction of nitric acid to, by the galvanic current, 403.
Ammonio-copper ammonium cyanide, 420.
Ammonium barium imidosulphonate, TRANS., 966.
—— calcium imidosulphonate, TRANS., 968.
—— chloride, action of, on silicates, at its dissociation temperature, 772.
—— —— influence of ammonia on the solubility of, 276.
—— diaminechromium thiocyanate, 798.
—— dithionate hydrochloride, 13.
—— ethyl sulphate, 700.
Ammonium fluoroxyhypovanadate, 787.
—— fluoroxyvanadates, 785.
—— imidosulphonates, TRANS., 946.
—— isobutyl sulphate, 701.
—— manganese chloride, 781.
—— methyl sulphate, 700.
—— nitrate, explosion of, 683.
—— nitride, 113.
—— orthotolylimidodiacetate, 1335.
—— pentasodium imidosulphonate, TRANS., 961.
—— pyrosulphate, TRANS., 948.
—— salts, direct absorption of, by plants, 229.
—— sodium hydrogen imidosulphonate nitrate, TRANS., 962.
—— stannibromide, 121.
—— sulphate, formation of, by burning coal gas, 1389.
—— —— mineralising influence of, 1399.
—— tetraminechromium thiocyanate, 799.
Ampelochroic acids, α-, β-, and γ-, 1242, 1243.
Amphiglyoxime, chlor-, 693.
Amyl alcohol, formation of, from starch by a bacterium, 90.
—— alcohols, action of bromine on, 809.
—— phenylamidoacetate, 468.
Amylacetylene, normal, 1064.
Amylamine, ϵ-chlor-, 717.
—— hydrogen diaminechromium thiocyanate, 1000.
Amylamylenamine, 804.
Amylenehydroxynaphthaquinone, TRANS., 611.
Amylfurfurylcarbamide, 43.
Amylmethylacetylene, 1065.
Amyloid, vegetable, 803.
Amyrilines, 288.
Amyrinoxime, α-, 290.
Amyrins, α- and β-, hydrocarbons from, 288.
—— —— —— oxidation products of, 290.
Amyrone, α-, 290.
Amyrone, β-, 290.
Amyroneoxime, β-, 290.
Anæmia, tropical, 363.
Analcime as rock forming material, 1413.
Analgen, 1104.
Analysis, combination of wet and dry methods in, 100.
—— elementary, new drying apparatus for, 657.
—— gravimetric, simple and rapid method of, 524.
—— of liquids, application of capillary phenomena to, 236.

Analysis, organic, new method of, 753.
—— quantitative, new methods of, 103, 538.
—— —— use of bromic acid in, 910, 1027.
—— —— use of iodic acid in, 1027.
Anemonic acid, 1241.
Anemonin, 1241.
Anemoninic acid, 1241.
Angelic acid, constitution of, 1304.
Angostura bark, constituents of, 642.
Angosturin, 744.
Anhydrobenzenesulphoneorthamidobenzamide, 334.
Anhydrocinnamaldehydanisidine, 1195.
Anhydro-derivatives of citric and aconitic acids, Trans., 1033.
Anhydroecgonine, constitution of, 360.
Anhydroformaldehydaniline, 1190.
Anhydrometanitrocinnamaldehydanisidine, 1195.
Anhydrotricarballylic acid, 41.
Anhydrovaleraldehydaniline, 1193.
Anilacetone, isonitroso-, 985.
Anilbenzoïn, action of hydrocyanic acid on, 1196.
Anilcyanamide, 1323.
Anilic acid, decomposition products of, 834.
—— acids, substituted, crystalline forms of the sodium salts of, Trans., 581.
Anilides, acid, colour reactions of, 709.
—— isoanilides and their analogues, 705.
Anilidobenzenemetadisulphonic acid, 333.
Anilidobenzenesulphonic acid, metanitro-orsho-, 332.
—— —— metanitropara-, 331.
Anilidobromopianic acid, 1209.
Anilidocinnoline, 1494.
Anilidodiphenylpyrrolone, 1002.
Anilidoisobutyric acids, 1338.
Anilidoisovaleramide, α-, 1192.
Anilidometanitrobenzophenone, ortho-, 336.
—— para-, 336.
Anilidometasulphobenzoic acid, ortho-, 333.
—— —— para-, 333.
Anilidometamidobenzenesulphonic acid, ortho-, 332.
—— —— para-, 332.
Anilidonaphthoic acid, β-, 1476.
—— anilide, β-, 1476.
Anilidonitrobenzanilide [2 : 5], 326.
Anilidoparadiketohexene, pentachlor-, 448.
Anilidopropionic acid, α-nitroso-, 1456.
Anilidopropionic acid, β-, 1342.
Anilidotetraphenylpyrroline, 995.
Anilidotrinitrotoluene, sodium derivative of, 1218.
Aniline, action of trimethylene chlorobromide on, 1491.
—— and furfuraldehyde, condensation of, 1452.
—— hydrogen diaminechromium thiocyanate, 1000.
—— nitrodibrom-, 1205.
—— orthonitro-, preparation of, 837.
—— platinothiocyanate, 287.
—— refractive power of, at different temperatures, Trans., 301.
—— thionylthio-, 1326.
Anilineazo-α-naphthol, ethyl and methyl ethers of, 862.
Aniline-black, dyeing with, in the dry way, 323.
Anilinesulphonic acids, parachlor- and parabrom-, constitution of, Proc., **1892**, 40.
Anilpyruvic acid, condensation of, 54.
Animal economy, action of oxalic acid and its derivatives on the, 1018.
—— —— change of sulphanilic acid into sulphanilocarbamic acid in the, 903.
—— organism, mechanism of the production of urea in, 89.
Anisodus luridus, alkaloïds of, 232.
Anisoïl, dinitrodiamido-, 596.
—— sulphonic acids derived from, Proc., **1892**, 90.
—— tetramido-, 596.
Anniversary meeting, Trans., 474.
Anodonta cygnea, blood of, 648.
Ant oil, composition of, 948.
Anthracene, action of nitric acid on, Trans., 865.
—— action of nitric acid on, in presence of acetone, Trans., 871.
—— action of nitric acid on, in presence of ether, Trans., 872.
—— action of nitric acid on, in presence of trimethylcarbinol, Trans., 870.
—— benzyl nitrate, Trans., 871.
—— isobutyl nitrate, Trans., 867.
—— propyl nitrate, Trans., 866.
Anthranilamide, dichlor-, 335.
Anthrax, chemical pathology of, 744.
—— in man, 1117.
Anthrole, nitro-, Trans., 869.
Anthrone, nitro-, Trans., 865, 868.
—— —— action of alcoholic potash on, Trans., 869.
Anthyllis vulneraria, composition of, 522.
Antiglyoxime, chlor-, 694.
Antimonious chloride, solution of, in saturated solutions of sodium chloride, 413.
—— compounds, estimation of, 526.
Antimonite from Felsöbánya, 1054.

Antimonite from Magurka, 1054.
Antimony, action of nitric acid on, 1402.
—— arsenic and tin, detection of, 918.
—— —— —— separation of, Trans., 424.
—— double halogen salts of, 788.
—— electrolytic detection of, 541.
—— estimation of, 242.
—— hydrosulphide, Trans., 133.
—— lowering of the freezing point of bismuth by, Trans., 896.
—— lowering of the freezing point of cadmium by, Trans., 901.
—— lowering of the freezing point of lead by, Trans., 908.
—— minerals, assay of, 918.
—— separation of, from arsenic, 541.
—— sodium alloy, 773.
—— sulphide, colloïdal solutions of, Trans., 142.
—— thiophosphate, 413.
Antipyrine, action of sodium and carbonic anhydride on, 1106.
—— alcohol of, 708, 730, 1106.
—— nitro-, 730.
—— paralkyloxy-derivatives of, 1080.
Apionyloximidoacetic acid, 328.
Apoatropine, 1255.
Apocinchonine, 1253.
Apple tree leaves, analyses of, 1372.
Arabinose, fermentation of, with *Bacillus ethaceticus*, Trans., 737.
—— physiological action of, 1506.
—— reactions of, 290.
—— thermochemistry of, 763.
Arabitol, thermochemistry of, 764.
Arctic Ocean, water from the, 1287.
Areca nut, alkaloïds of the, 737.
Arecaïdine, 739.
Arecoline and its salts, 738.
Argentic disodium imidosulphonate, Trans., 976.
Aristolochia argentina, alkaloïd from, 894.
—— *reticulata*, volatile oil from, 70.
Aristolochin, 874.
Aristolochine, 894.
Aromatic compounds, unsaturated, action of nitrous acid on, 447.
Arsenic acid, separation of, from mercury, sodium, chlorine, and nitric acid, 530.
—— —— thio-, and thioxyarsenic acid, separation of, 1519.
—— —— volumetric estimation of, 1519.
Arsenic, allotropic states of, 405.
—— antimony and tin, separation of, Trans., 424.
—— cyanide, 1164.
—— direct estimation of, in minerals and metals, 530.
Arsenic, electrolytic separation of gold from, 920.
—— estimation of, by oxidation with the electric current, 752.
—— estimation of, in wall paper, 382.
—— hydrosulphides, Trans., 127.
—— lowering of the freezing point of bismuth by, Trans., 894.
—— lowering of the freezing point of cadmium by, Trans., 899.
—— lowering of the freezing point of lead by, Trans., 906.
—— separation of antimony from, 541.
—— testing metallic iron for, 1030.
Arsenious acid, volumetric analysis with, 1374.
—— compounds, estimation of, 526.
—— sulphide, colloïdal solutions of, Trans., 140, 144, 160.
Arsines, tertiary, action of benzal chloride on, 984.
Artemisia absinthium, absinthin from, 1240.
Artichoke, Jerusalem, composition and cultivation of, 1024.
—— —— cooked, composition of, Trans., 227.
Asaprol, 1116.
Asbestos, use of, in filtration, 751.
Asbolin, 1312.
Ascharite, a new borate, 792.
Asparagine, decomposition of, in the human body, 904.
—— influence of carbohydrates on the accumulation of, in plants, 91.
Aspergillus niger, action of, on fumarates and maleates, 820.
Asphalt in Utah and Colorado, 21.
Asphyxia, effect of, on the glycolytic and saccharific powers of the blood, 517.
Assimilation of atmospheric nitrogen, 1507.
—— of carbohydrates, 742.
Astacus fluviatilis, blood of, 648.
Astragalus, analyses of, 522.
Astrophyllite, new analyses of, 22.
Atmosphere, estimation of organic matters in, 542.
—— estimation of the carbonic anhydride of, 533.
—— of the Tropics, ammonia in, 381, 909.
Atomic weight and magnetism, 672.
—— —— of boron, Trans., 650.
—— —— of cadmium, 1397.
—— —— of cobalt, 1159.
—— —— of nickel, 1158.
—— —— of oxygen, 1388.
—— —— of palladium, Trans., 745.
—— weights, relations between, 938.

Atropa belladonna, alkaloïds of, 231.
Atropamine, 1256.
Atropine, detection of, 1534.
—— nitro-, 1014.
Atropine, ψ-, 891.
Aurantiol, 868.
Auric sulphide, properties and reactions of, 280.
Aurin, acetyl derivatives of, 1319.
Aurintricarboxylic acid, 855.
Autocatalysis, 1270.
Axinite, formula of, 125.
Azimidazoles, 313.
Azines of the uric group, 70.
Azobenzene, dinitroso-, 1079, 1198.
—— —— preparation of, 1321.
—— —— so-called, 889.
—— nitronitroso-, reduction of, 1322.
Azobenzenedisulphonamide, 973.
Azobenzenemetachlorophenylhydrazine,
—— trinitro-, 456.
—— trinitronitroso-, 455.
Azobenzeneorthocarboxylic acid, 67.
—— —— parachlor- and parabrom-, 68.
Azobenzenephenylhydrazine, nitro- and chloronitro-derivatives of, 455.
Azo-colours, alkylated, of the naphthalene series, reduction of, 862.
Azo-compounds, condensation of aldehydes with, 854.
—— —— mixed, 710.
—— —— nitroso-, constitution of, 1453.
—— —— oxidation of, 48.
—— —— reduction products of, 839.
Azodibenzylamine, ortho-, 316, 890.
Azodicarbonamide, 1298.
—— preparation of, 1430.
Azodicarbonamidine salts, 1297.
Azodicarboxylic acid, 1429.
Azo-group, intramolecular formation of, 316.
—— —— substitution of, for ketonic oxygen, 451.
Azoimide, 112.
—— action of, on living organisms, 90.
—— heat of formation of, 261.
—— thermochemistry of, 933.
Azoisatin, 451.
Azomethylquinoline, 729.
Azonium bases, 1246.
—— compounds, 1108.
Azotoluenedisulphonamide, 1468.
Azoximes, 135, 317.
Azoxymethylethylisoxazole, 79.
Azoxymethylquinolines, 727, 729.
Azoxyorthodichlorostilbene, para-, 444.
Azoxyphenetoïl, para-, 159.

B.

Bacillus amylozymicus, 90.
—— *ethaceticus*, fermentation of arabinose with, Trans., 737.
—— —— fermentation of mannitol and dextrose with, Trans., 442.
—— *ethacetosuccinicus*, fermentation of mannitol and dulcitol by, Trans., 254.
—— —— morphological characterisation of, Trans., 275.
—— of malignant œdema, action of, on carbohydrates and on lactic acid, 91.
—— *radicicola*, accumulation of atmospheric nitrogen in cultivations of, 1019.
Bacteria, soluble colouring matters produced by, in distilled medicinal waters, 907.
Bacterium which ferments starch and produces amyl alcohol, 90.
Balance, modified, for rapid weighing, 270.
Balance sheet of the Chemical Society, from March 19th, 1891, till March 18th, 1892, Trans., 484.
—— —— of the Research Fund, from March 19th, 1891, till March 18th, 1892, Trans., 485.
Barium acetothiosulphate, 1419.
—— ammonium phosphotungstates, 1160.
—— and calcium, separation of, 915.
—— carbide, 685.
—— estimation of, 539.
—— hydrogen imidosulphonate, Trans., 965.
—— hypophosphate, 403.
—— imidosulphonate, Trans., 964
—— isophthalate, composition and crystalline form of, 179.
—— mercury imidosulphonate, Trans., 977.
—— nitride, 566, 776.
—— oxide, non-existence of dimorphism in, 17.
—— permolybdate, 1160.
—— peroxide, action of, on metallic salts, 408.
—— —— use of, in analysis, 1031.
—— barium persulphate, 12.
—— potassium imidosulphonate, Trans., 967.
—— separation of, from calcium, 100.
—— sodium imidosulphonate, Trans., 967.
—— strontium and calcium, separation of, 660.
—— sulphamate, Trans., 966.
—— thiocyanate, water of crystallisation of, 1418.

Barium, volumetric estimation of, 1521.
Barium-group, analysis of, 660.
Bark of trees, calcium oxalate in the, 1370.
Barks, estimation of gallotannic and gallic acids and tannin in, 390.
Barley, distribution and condition of iron in, 1509.
Barytes from Missouri, 792.
Basalt of the Stempel, near Marburg, 126.
Bases and acids, study of the chemical neutralisation of, by means of their electrical conductivities, 2.
—— organic, action of ethyl cyanacetate on, 1071.
—— —— chloriodides of, 1356.
—— —— method of determining the number of imido-groups in, PROC., **1892**, 133.
—— Schiff's, 1189.
Baths, hot, influence of, on the excretion of nitrogen and uric acid from the human system, 1503.
Batteries, gas, E.M.F. of, 393.
—— secondary, theory of, 1381.
Beans, broad and haricot, cooked, composition of, TRANS., 227.
Bebeerine, reactions of, 756.
Beer and beer wort, estimation of maltose, dextrose, and dextrin in, 248.
Beeswax, analysis of, 1034.
—— assay of, for vegetable wax, 551.
—— detection of resin in, 923.
—— examination of, 251.
Beet diffusion chips, frozen and unfrozen, composition of, 1512.
Beet juice, organic acids in, 231.
Beetroot, cooked, composition of, TRANS., 227.
Behenolic acid, action of reducing agents and of bromine on, 812.
—— —— diiodo-, 471.
—— —— tetrachloride of, 1427.
—— anilide, 1427.
—— diphenylhydrazide, 1427.
—— phenylhydrazide, 1427.
Belladonna, alkaloïds of, 1498.
—— subsidiary alkaloïds of, 1255.
—— wild, alkaloïds of, 231.
Benzal chloride, condensation of with benzene, 719.
Benzalamidoguanidine, 1297.
Benzaldehyde, action of, on 2 : 6-lutidine, 1360.
—— action of sodium on, 171.
—— action of zinc and ethyl chloracetate on, 1300.
—— and ethyl cyanacetate, condensation of, 1086.
—— hydrazone, TRANS., 788.
—— orthamido-, condensation of, 1106.
Benzaldehyde, parabromometanitro-, 336.
—— paranitro-, change of, in the system, 1504.
Benzaldehydephenylhydrazone, orthamido-, 1106.
Benzaldiphenylmaleïde and its derivatives, 179, 483.
—— bromo-, 483.
Benzaldiphenylmaleïmidine, 484.
—— nitro-, 487.
Benzaldiphenylmaleïnethylimidine, 484.
Benzaldoxime, synorthochloro-, 1200.
Benzaldoximes, orthochloro-, 1199.
—— α- and β-paranitro-, 163.
Benzalglucoheptitol, 1168.
Benzalhydrazine, 456.
Benzalsemicarbazide, 1297.
Benzamide 2 : 5-amidonitro-, 326.
—— orthamido-, action of sulphonic chlorides on, 334.
—— —— thio-derivatives of, 54.
—— physiological action of, 367.
—— thio-, action of iodine on, 1109.
Benzamidoxime benzyl ether, 464.
Benzene, action of acetic and benzoic chlorides on halogen derivatives of, 337.
—— and dipropargyl, 1436.
—— chloro-, action of bromine on, TRANS., 111.
—— chloropentabromo-, 155.
—— condensation of, with benzal chloride, 719.
—— constitution of, 1211.
—— dichlorotetrabromo-, 155.
—— dinitro-, physiological action of, 366.
—— dinitrochloro-, action of, on polyhydric phenols, 310.
—— flames, experiments on, TRANS., 209, 210.
—— hexabromide, preparation of, TRANS., 110.
—— hexachloride, chloro-, α- and β-modification of, TRANS., 103.
—— —— —— action of potassium cyanide on, TRANS., 108.
—— —— reduction of, 594.
—— iodation of, 1310.
—— metadinitro-, 704.
—— —— bromination of, 155.
—— —— reduction of, 595.
—— penta-, derivatives of, 596.
—— ring, displacement of halogen atoms in the, 335.
—— rule for determining whether a given mono-derivative of, shall give a meta-di-derivative or a mixture of ortho- and para-di-derivatives, TRANS., 367.

Benzene, symmetrical trinitro-, bromination of, 155.
—— tetrachlorodibromo-, 155.
—— triamidotrinitro-, symmetrical, reduction of, 1198.
—— tribromonitro-, 1182.
—— unsymmetrical tetrachloro-, properties of, TRANS., 109.
Benzeneazocyanocamphor, 1343.
Benzeneazo-β-naphtholdisulphonic acid, oxidation of, 48.
Benzeneazo-α-naphthylglycocine, 191.
—— —— meta-, ortho-, and para-nitro-, 1100.
Benzeneazoparacresol, metachloro-, 975.
—— parachloro-, 974.
Benzeneazoresorcinol, para-, 977.
Benzeneazo-β-tolylnaphthylamine, 1476.
Benzenediazoacetanilide, 458.
Benzeneindone, 341.
Benzenemetadisulphonic acid, amido-, 333.
Benzenes, iodo-, 1310.
—— nitro-, heats of combustion and formation of, 4.
—— —— displacement of the nitro-group in, by chlorine or bromine, 306.
Benzenesulphinic acid, parabromo-, 1091.
Benzenesulphonamides, and mixed secondary amines, 64.
Benzenesulphonebenzylamide, 65.
Benzenesulphonemethylethylamide, 64.
Benzenesulphoneorthamidobenzamide and its derivatives, 334.
Benzenesulphoneorthamidobenzomethylamide, 335.
Benzenesulphoneorthamidobenzophenylamide, 335.
Benzenesulphoneorthamidobenzoylphenylhydrazine, 335.
Benzenesulphoneorthomethamidobenzamide, 335.
Benzenesulphoneorthotoluidine, 65.
Benzenesulphoneparaphenetidine, 65.
Benzenesulphonepiperidine, 65.
Benzenesulphonic acid, metanitro-orthamido-, 331.
—— —— metanitroparamido-, 331.
—— —— nitroso-, preparation and salts of, 475.
—— acids, chloramido- [1 : 2 : 4 and 1 : 4 : 2], 182.
—— —— chloronitro- [1 : 2 : 4 and 1 : 4 : 2], 182.
—— —— halogenated, action of ammonia and aniline on, 331
—— chloride, parabromo-, 1220.
—— —— parachloro-, 1220.
Benzenesulphonitramide, 850.
Benzenethiosulphonic acid, reactions of, 478.
Benzenylamidethoxime, action of nitrous acid on, 323.
Benzenylamidine picrate, 705.
—— salts, 51.
Benzenylchloroxime, 463.
—— paranitrobenzyl ether, 464.
Benzenylchloroximeglycollic acid, 465.
Benzenyldiamidoacetone, 952.
Benzenylethoxime salts, 323.
Benzenylhydrazoximamidobenzylidine, preparation of, 461.
Benzenylimidosulphonic acid, 701.
Benzenylnitrotoluylenamidine, 1197.
Benzenylorthohomosalicenylazoxime, 320.
Benzenylparahomosalicenylazoxime, 319.
Benzhydroxamic acid, stereoisomeric derivatives of, 461.
Benzide, diamidosulpho- and its derivatives, 1093.
Benzidine, polymethylene bases from, 1223.
Benzidinedisulphonamide, 974.
Benzidinemetacarboxylic acid, 68.
Benzidylbromopianic acid, 1210.
Benzile, action of aniline on, 1470.
—— action of, on triamidodiphenylamine, 1109.
—— action of paramidodimethylaniline on, 855.
—— sodium derivative of, 171.
Benziledianil, 1470.
Benzileoximeanil, 1470.
Benzileoximehydrazone, 1471.
Benzileoximeparatolyl, 1470.
Benzileoximes, 1470.
—— Claus' theory of the, 186, 598.
Benzilideneamidocarbazole, 616.
Benzilidenebenzidine, nitro-derivatives of, 854.
Benzimidazoles, 631, 632.
Benzimido-β-chlorethyl ether, 1331.
Benzofurfuran derivatives, synthesis of, 608.
Benzoic acid and benzaldehyde, condensation of, 339.
—— —— 2 : 5-bromonitro-, amide, anilide, and chloride of, 326.
—— —— 2 : 4-chloronitro-, chloride, amide, and anilide of, 327.
—— —— impurities in commercial, 604.
—— —— iodoso-, 1460.
—— —— nitrosulpho-, 479.
—— —— parabromo-, iodation of, 714.
—— —— parabromometanitro-, salts of, 714.
—— —— separation of salicylic acid from, 1532.

Benzoic acids, amido-, reactions of, 847, 1380.
—— —— bromo-, bromination of, 171.
—— —— dibromo-, 1205.
—— —— dichloro-, 1206.
—— —— halogenated nitro-, action of ammonia and aniline on, 326.
Benzoïn, action of paradiamidodimethylaniline on, 855.
Benzonitrile, action of benzoic chloride on, 1183.
—— action of sulphuric anhydride on, 713.
—— compound of, with hydrogen cyanide, 1449.
Benzonitriles, dibromo-, 1205, 1206.
—— dichloro-, 1206.
Benzoparadifurfuran-α-dimethyl-β-dicarboxylic acid, paradichloro-, 610.
Benzophenone, diparabromodimetanitro-, 336.
—— diparabromometanitro-, 336.
—— imido-, hydrochloride, 339.
—— orthbromo-, 992.
—— orthobromometanitro-, 336.
—— parabromometanitro-, 336.
—— paradinitro-, 1460.
—— paramido-, oximes of, 489.
—— paramidometanitro-, 336
—— paramidometanitroparabromo-, 336.
—— sodium compound of, 170.
Benzophenone-derivatives, oximes of, 487.
Benzophenoneparamidobenzoic acid, 340.
Benzotoluidide, paranitro-, 839.
—— thionitro-, 839.
Benzoyl compounds, preparation of, 604.
Benzoylacetamide, 325.
Benzoylacetone, acids from the dicyanhydrin of, 1471.
—— action of paramidodimethylaniline on, 855.
—— magnetic rotation of, Trans., 831, 861.
Benzoylaconine, formation of, Trans., 401.
Benzoylamidocarbazole, 616.
Benzoylbenzamide, metanitro-, 52.
Benzoylbenzeneazoacetone, 977.
Benzoylbenzenehydrazo-orthocresol, 975.
Benzoylbenzylmetaxylidine, 1320.
Benzoylbenzylparatoluidine, 313.
Benzoylchlorophenols, isomeric, 308.
Benzoyldihydroxyanhydroecgonine, derivatives of, 1016.
Benzoyldiorthotolylhydrazine, 843.
Benzoyldiphenylhydrazide, 711.
Benzoyldiphenylhydrazine, 843.
Benzoylformorthotoluidide, 1442.
Benzoylglutarimidoxime, 138.
Benzoylhydrochlorocarvoxime, 1348.
Benzoylimidopropionylethyl cyanide, derivatives of, 450.
Benzoylisoeugenol, 46.
Benzoyllimonene nitrosochloride, 1348.
Benzoylmetachlorobenzeneazoparacresol, 975.
Benzoylmetachlorobenzenehydrazoparacresol, 975.
Benzoylmethyltrimethylene, Trans., 86.
Benzoylmethyltrimethylenecarboxylic acid, Trans., 84.
—— —— oxime of, Trans., 85.
Benzoyl-α-naphthylhydrazine, 509.
Benzoylnicotenylamidoxime, 207.
Benzoylnitrosoresorcinol ethyl ether, 45.
Benzoylorthamidophenylacrylic acid, 881.
Benzoylorthotolylcarbamide, 832.
Benzoylorthotolylhydrazine, 843.
Benzoyloscine, 1498.
Benzoylparabromanilide, 460.
Benzoylparachlorobenzeneazoparacresol, 975.
Benzoylphenylazomethylene, reactions of, 451.
Benzoylphenyldiiodomethane, 451.
Benzoylpropionic acid, oximes of, 1202.
Benzoyl-α-pyridyllactic acid, 76.
Benzoyl-β-pyridyllactic acid, 78.
Benzoylpyruvic acid, oxime of, 304.
Benzoylretene, 1205.
Benzoylsuccinimidoxime, 137.
Benzoylsulphobenzamidinic anhydride, 713.
Benzoyltetrahydroquinaldine, nitroderivatives of, 882.
—— oxidation of, 881.
Benzoylthiocarbimide and aldehydeammonia, Trans., 532.
Benzoyltrimethylene oxime, Trans., 86.
Benzoylxylide, 491.
Benzyl alcohol, paramidorthochloro-, 445.
—— —— paranitrorthochloro-, 445.
—— bromide, paranitrorthochloro-, derivatives of, 444.
—— dinitrosylorthochloro-, 1200.
—— ethyl ether, paranitrorthochloro-, 445.
—— hydroxycamphocarboxylate, 74.
—— imidodicarbothioxylate, 844.
—— imidodiphenylthiocarbamate, Proc., 1892, 97.
—— metaxylyl ketone, 338.
—— methyl ether, paranitrorthochloro-, 444.

Benzyl orthotoluate, action of sodium on, Proc., **1891**, 167.
—— orthotolylcarbamate, 832.
—— ortho-xylyl ketone, 338.
—— paraxylyl ketone, 338.
—— phenylimidophenylbenzylthiocarbamate, Proc., **1892**, 97.
Benzylacetanilide, orthamido-, 80.
Benzylacetoglutaric acid, 963.
Benzylacetomethylamide, diorthonitro-, 218.
—— orthamido-, 218.
Benzylamidoacetic acid, benzylamide of, 1458.
Benzylamidosulphonic acid, 476.
Benzylamine, action of carbonyl chloride on, 312.
—— and furfuraldehyde, condensation of, 1452.
—— di-iodo-, 1449.
—— diorthonitro-, 218.
—— hydrogen malate, action of heat on, 820.
—— orthonitro-, 217.
Benzylaniline, paranitrorthochloro-, 445.
Benzylbenzenylamidine, 1110.
Benzylbenzyl ortho-xylyl ketone, 338.
Benzylbenzylhydroxylamine, nitro-, oxidation of, 1456.
Benzylborneols, 73.
Benzylbornylamine, 1238.
Benzylcamphor, 73.
Benzylcamphoroxime, 73.
Benzyl-δ-caprolactone, γ-, 963.
Benzylcarbamide, orthonitro-, 218.
Benzylchrysaniline, 1095.
Benzylcinchonidine, 1251.
Benzyldihydroxycinchotenidine, 1251.
Benzydihydroxycinchotenine, 1250.
Benzyldiphenylmaleïde and its derivatives, 484.
Benzyldiphenylmaleïmidine, 484.
Benzyldiphenylmaleïnethylimidine, 485.
Benzyldiphenylthiourea, Proc., **1892**, 97.
Benzylethylparatoluidine, 313.
Benzylethylphenylthioureas, isomeric, Trans., 540.
Benzylfenchylamine, 1239.
Benzylfumaramic acid, 821.
Benzylfumarimide, 821.
Benzylfurfuraldoxime, 1434.
Benzylhydroxyanthranol, 346.
Benzylhydroxycaproic acid, salts of, 963.
Benzylhydroxydiphenylmaleïde, 483.
Benzylhydroxylamine, β-chloro-, 1200.
—— β-dichloro-, 1199.
—— β-metanitro-, 51.
Benzylhydroxylamines, oxidation of, 316.
Benzylidenebornylamine, 1238.
Benzylidenecinchonic acid, 1489.
Benzylidenecinchoxinic acid, 1489.
Benzylidenecyanacetic acid, 1340.
Benzylidenediphenylsulphone, 612.
Benzylidenefenchylamine, 1239.
Benzylidene- 2 : 6-lutidine, 1360.
—— reduction of, 1361.
Benzylideneorthamidophenol, 196.
Benzylideneparamidophenol, 1451.
Benzylideneparanitraniline, 1194.
Benzylidenepinylamine, 997.
Benzylidenepiperazine, 211.
Benzylidenethiophenylhydrazone, 1326.
Benzylisobenzaldoxime, metanitro-, 50.
Benzylisobutylcarbamide, 312.
Benzylisometanitrobenzaldoxime, intramolecular change of, 50.
Benzyliso-orthochlorobenzaldoxime, orthochloro-, 1199.
Benzylisoparanitrobenzaldoxime, intramolecular change of, 50.
Benzylmalamic acid, 822.
Benzylmalimides, α- and β-, 821.
Benzylmalonic azimide, Trans., 796.
—— phenylhydrazide, Trans., 796.
Benzylmetanitrophenylcarbamide, 312.
Benzylmetaxylidine, 314.
—— nitro-, 1320.
Benzylmetaxylidinesulphonic acid, 1320.
Benzylmethylamine, diorthonitro-, 218.
Benzylmethylparatoluidine, 313.
Benzyl-α-naphthylcarbamide, 312.
Benzylnitrobenzylhydroxylamine, oxidation of, 1456.
Benzylœnanthaldoxime, 1436.
Benzylorthotoluidine, 48.
Benzylorthotoluidinesulphonic acid, 313.
Benzylparachlorodeoxybenzoïn, 1227.
Benzylparaditolylcarbamide, 1083.
Benzylparatoluidine, 313.
—— hydrochloride, orthamido-, 734.
Benzylparatolylcarbamic chloride, 1083.
Benzylparatolylsemithiocarbazide, Trans., 1022.
Benzylpentoxazoline, μ-, 215.
Benzylphenylhydrazine, orthamido-, 1455.
—— orthonitro-, 1455.
—— phosphenite, 1325.
Benzylphenylhydrazone, thionyl-, 1324.
Benzylphenylmethylcarbamide, 312.
Benzylphenylsemithiocarbazide, Trans., 1021.
Benzylpiperidylcarbamide, 312.
Benzylquinoline-γ-carboxylic acid, betaïne of, 1488.
Benzylsulphonethiobenzylmethylmethane, 613.
Berbamine, 641.
Berberine, 1498.

Berberine, action of bromine on, 1498.
—— pyridinecarboxylic acids from, 1357.
—— salts, 642.
Berberis alkaloïds, 641, 1498.
Berberis aquifolium, constituents of, 641.
—— *vulgaris*, alkaloïds of, 641.
Berberonic acid, 1357.
Bergamot oil, 868, 1235.
—— —— crystalline products from, 349.
—— —— stearoptene of, 71.
Bergapten, the stearoptene of bergamot oil, 71.
Beronic acid, 1357.
Beryllium hypophosphates, 404.
Betaïne in cotton-seed foods, 380.
Betel oil, composition of, 833.
Betelphenol, 833.
Biazolones, 508.
Biguanide, preparation of, from guanidine, 737.
Bile during inanition, 225.
—— ox, presence of myristic acid in, 1114, 1503.
—— putrefaction of, 518.
Birotation of sugars, influence of ammonia on, 1419.
Bis-α_1-keto-γ_1-methyljulolidyl, 497.
Bismuth, action of nitric acid on, 1403.
—— and cadmium, separation of, by means of bromine vapour, 385.
—— and lead, separation of, by means of bromine vapour, 540.
—— chloride, dissolution of, in a saturated solution of sodium chloride, 122.
—— double halogen salts of, 788.
—— estimation of, 539.
—— estimation of, in silver slags, 919.
—— hydrosulphide, attempts to prepare, Trans., 132.
—— lead, tin, and cadmium, separation of, 754.
—— liquid, thermal expansion of, 259.
—— lowering of the freezing point of cadmium by, Trans., 904.
—— lowering of the freezing point of lead by, Trans., 910.
—— lowering of the freezing point of, when alloyed with other metals, Trans., 888, 892.
—— pure, 20.
—— salicylate, 122.
—— separation of, from lead, 385.
—— sodium alloy, 773.
—— tribromide, action of hydrogen phosphide on an ethereal solution of, 279.
Bismuthic acid, 413, 688.
Bismutite, 793.
Bis-1 : 2 : 3-phenylbenzoylmethylpyrazolone, 146.
Biurets, thio-, 703.
Bleaching powder, estimation of active chlorine in, 1374.
Blende, separation of lead, silver, and zinc in, 1378.
Blood, action of carbon bisulphide on, 1520.
—— coagulation of the, 87, 1112.
—— detection of, 1369.
—— disappearance of sugar from the, 363.
—— dissolved nitrogen in, 1257.
—— estimation of the glycogen in, 89.
—— fermentation of, 900.
—— formation of sugar from peptones in, 1502.
—— glycolysis in, 900.
—— glycolytic power of, 364.
—— of a living mammifer, absorption of carbonic oxide by, 743.
—— of Europeans living in the tropics, sp. gr. of, 363.
—— of invertebrates, 648.
—— of leucæmic patients, peptones in the blood of, 519.
—— of *Pinna squamosa*, 1016.
—— of the crustaceæ, blue colouring matter of, 898.
—— peptone, gases of, 363.
—— serum, human, new proteïd from, 224.
—— sugar in, 743.
—— toxic action of, 228.
—— variations of the glycolytic and saccharific powers of, in asphyxia and diabetes, 517.
Blood-ash, influence of nutrition on the composition of, 225.
Body, human, decomposition of fibrin, gelatin, peptone, and asparagine, in the, 904.
Boehmeria, composition of, 1511.
Boiler incrustation, composition of a, 17.
Boiling point curves for the normal paraffins, 947.
—— points of acids and alcohols, mechanical determination of, 1039.
—— —— of compounds with complex terminal substitution, mechanical determination of, 1039.
—— —— of compound of simple terminal substitution, mechanical determination of, 948.
—— —— of normal isomeric ethereal salts of the fatty series, calculation of, 260.
—— —— of paraffin derivatives, calculation of, 797.

Boiling points of solutions of metallic chlorides, TRANS., 340.
Boleite, 123.
Bcletus edulis and *B. aurantiacus*, distribution of sugars in, 519.
Bone-black, iron in, 1053.
Bones, fossil, of various ages, proportion of fluorine in, 1413.
—— influence of various salts on the composition of, 647.
—— recent and fossil, fluorine in, 1161.
Borates, metallic, 404, 565.
Boric acid, action of, on germination, 651.
—— —— and mannitol, freezing points of aqueous solutions of, 263.
—— —— estimation of, 384.
—— —— influence of, on the electrical conductivity of dilute alcoholic solutions of organic acids, 1265.
—— —— presence of, in the products of the soil, 93.
Borneocamphene, 624, 625.
Borneol, constitution of, 865.
Bornyl ethyl ether, 200, 348.
—— methyl ether, 348.
—— methylene ether, 200, 348.
Bornylamine tartrate, 1238.
Boron, action of, on organic halides, 1316.
—— amorphous, preparation of, 681, 682.
—— —— properties of, 1153.
—— atomic weight of, TRANS., 650.
—— bromide, combination of ammonia with, 771.
—— —— preparation of, TRANS., 655.
—— iodide, 1154.
—— —— combination of ammonia and of hydrogen phosphide with, 771.
—— nitride, action of methyl alcohol on, 1311.
—— pentasulphide, 1394.
—— phosphides, 115, 272, 273.
—— phosphodi-iodide, 114.
—— phosphoiodide, 115.
—— trisulphide, 1392.
Bran, distillation of, with lime, PROC., **1892**, 138.
Brandy, presence of a tetracarbon aldehyde in, 810.
Brasileïn, derivatives of, 502.
Brasilin, oxidation of, 502.
Brassidic acid and erucic acid, stereometric relations of, 429, 812, 1427.
—— —— bromo- and chloro-, 429.
—— —— dichloro-, 1427.
—— —— dichloride, 429.
—— phenylhydrazide, 1428.
Braunite from Sweden, 1404, 1405.
Breithauptite from Sarrabus, Sardinia, 790.
Bromanilic acid, action of halogens on 834.
—— —— crystalline form of the sodium salt of, TRANS., 582.
Bromic acid, use of, in quantitative analysis, 910, 1027.
Bromides, estimation of, 527.
—— of potassium, sodium, and hydrogen, action of sulphuric acid on, TRANS., 94.
Bromine and chlorine, detection of, in presence of iodine, 1514.
—— —— relative orienting effect of, PROC., **1892**, 40.
—— carriers of, 155.
—— chlorine, and iodine, exchange of, between inorganic and organic haloïd compounds, 574.
—— —— —— separation of, 1027.
—— direct combination of, with metals, 118.
—— heat of combination of, with magnesium, 762.
—— vapour, separation of metals of the hydrogen sulphide group by means of, 754.
Bromochloranilic acid, crystallography of the sodium salt of, TRANS., 584.
Bromoform, formation of acetylene from, 421.
—— preparation of, from acetone and sodium hypobromite, 126.
Brookite, 1055.
Brushwood, food value of, 1511.
Bulbocapnine, 1366.
Bunsen burner for spirit, 1386.
Bunte's salt, preparation and properties of, 799.
Burettes, improvements in, 1027.
Burner, new laboratory, 768, 1386.
Butaldehydes, condensation of, with aniline, 1192.
Butane, absorption-coefficient of, in water, 1043.
Butanetricarboxylic acid, 42.
Butter, acids of, 1113.
—— detection of coco nut fat in, 391.
—— detection of margarin in, 1034.
—— estimation of foreign fats in, 1532.
—— estimation of free acids in, 924.
Butyl alcohol, normal, action of bromine on, 809.
—— bromides, bromination of, 1414.
—— chlorides, chlorination of, 1415.
Butylamine, δ-chloro-, 131.
Butylbenzene, action of aluminium chloride on, 1309.
Butylchloralacetamides, 1067.
Butylchloralaldol, 695.
Butylchloralbenzamides, 1067.
Butylchloraldoxime, 33.
Butylchloralformamides, 1067.

Butylenes, monobromo-, 127.
Butylidenaniline, 1192.
Butylmetaxylene, tertiary, derivatives of, 718.
Butylmethylacetylene, 1064.
Butylparisopropyltoluene, ortho-, 985.
Butylphenol, paratertiary, 44.
Butyltoluenesulphonic acid, nitration of, 718.
Butylxylenesulphonic acid, nitration of, 718.
Butyramide, αβ-dibromo-, 27, 33.
Butyric acid, α-amido-, derivatives of, 1338.
—— —— αβ-dibromo-, 27, 33.
—— —— β-sulpho-, 424.
Butyrolactone, action of sodium ethoxide on, 813.
—— hydrolysis of, 1303.

C.

Cabbage, cooked, composition of, TRANS., 227.
Cadmium, action of nitric acid on, 1278.
—— and bismuth, separation of, 385.
—— and copper, separation of, 534.
—— and gold, compound of, TRANS., 914.
—— atomic weight of, 1397.
—— crystallisation of, 1398.
—— diaminechromium thiocyanate, 1002.
—— electrolytic separation of, from osmium and from nickel, 920.
—— fluorovanadite, 788.
—— fluoroxyhypovanadate, 787.
—— gold, and tin, estimation of, in alloys, 1030.
—— hydrosilicate, 1157.
—— hydrosulphide, TRANS., 129.
—— lead, tin, and bismuth, separation of, 754.
—— lowering of the freezing point of bismuth by, TRANS., 895.
—— lowering of the freezing point of lead by, TRANS., 907.
—— lowering of the freezing point of, when alloyed with other metals, TRANS., 888, 897.
—— mercuric cyanide, TRANS., 687.
—— mercuric thiocyanate, 10.
—— nitrate, basic, 1157.
—— oxide, action of hydrogen peroxide on, 1278.
—— sulphides, 778.
—— use of, in assaying gold, 919.
Cadmium-silver alloy, analyses of, TRANS., 913.
Cæsium antimony chloride, 788.
—— bismuth chloride, 789.
—— bromiodides, 773.
—— chloriodides, 773.
—— chlorobromides, 773.
—— chlorobromiodide, 773.
—— compounds, extraction of, from carnallite, 1395.
—— hydroxide, properties of, 274.
—— manganese chloride, 781.
—— reduction of, 274.
—— properties of, 274.
—— tribromide, 773.
—— triiodide, 773.
Calcium and barium, separation of, 100, 915.
—— and strontium nitrates, separation of, by means of amyl alcohol, 915.
—— —— separation of, as chromates, 914.
—— chlorate, rate of decomposition of, by heat, 1275.
—— chloride, boiling points of solutions of, TRANS., 340.
—— —— solutions, dilute, cryoscopy of, 1045.
—— chromate, solubility of, in dilute alcohol, 914.
—— estimation of, in gun-cotton, 1520.
—— estimation of, in phosphates, 534.
—— estimation of small quantities of, 914.
—— hydrogen imidosulphonate, TRANS., 968.
—— imidosulphonate, TRANS., 968.
—— iron, and manganese, separation of, 916.
—— metaborate, 404.
—— nitrate, basic, 1157, 1276.
—— —— cryoscopy of dilute solutions of, 1045.
—— nitride, 566.
—— oxalate in the bark of trees, 1370.
—— phosphate, crystalline, 407.
—— phosphates, solubility of, in solutions of phosphoric acid, 684.
—— potassium thiosulphate, 12.
—— salts, effect of, on the coagulation of the blood, 87, 1112.
—— —— estimation of, in syrup and sugar products, 1377.
—— sodium imidosulphonate, TRANS., 968.
—— strontium, and barium, separation of, 660.
—— volumetric estimation of, 1521.
Calorimetric bomb, modified form of, 260.
—— —— use of compressed oxygen in, 673.

Camphene, 868.
—— and camphoric acid, 868, 1240, 1481.
—— constitution of, 858, 868.
Camphenol, properties of, 199.
Campherylparatolylhydrazine, 1481.
Campherylphenylhydrazine, 1481.
Camphocarboxylic acid, 201.
Camphoic acid, constitution of, 866.
Campholamine, 1345.
Campholenic acid, 1237.
—— —— oxidation of, 1237.
—— —— reduction of, 1238.
Campholic acid, 1345.
—— —— action of potassium hypobromite on the amide of, 1345.
—— —— constitution of, 866.
Campholonitrile, 1345.
Campholyl isocyanate, 1345.
Campholylamine, 1346.
Campholylcarbamide, 1345.
Camphonitrile, 1237.
Camphor, action of sodium alkyloxides on, 72.
—— and fenchone series, 1236.
—— behaviour of, in mixtures of two solvents, 1137.
—— constitution of, 203, 724, 865, 869.
—— dibromo-, reactions of, 1343.
—— production of, 1 : 2 : 4-acetylorthoxylene from, Proc., **1891**, 188; **1892**, 54.
Camphoric acid, action of various reagents on, 1100.
—— —— and camphene, 868, 1240, 1481.
—— —— constitution of, 202, 348, 500, 627, 865, 869, 1041, 1100, 1346, 1347; Trans., 1096.
—— —— function of, 1346.
—— —— hydrazones of, 1481.
—— —— methyl salts of, Trans., 1088.
—— —— new acid from, Proc., **1892**, 55, 68.
—— —— thermochemistry of, 1041.
Camphor-group, 724, 1343.
Camphorone, 626; Proc., **1891**, 188; **1892**, 54.
Camphors and their compounds with chloral, physiological action of, 227.
Camphosulphophenols, ethylnitroketone and acetylnitroketone from, 1085.
—— nitroketone from, 999.
Cancer pagurus, blood of, 648.
Cantharene, 1480.
Cantharidin, action of phenylhydrazine on, 999.
Caoutchouc, spontaneous conversion of isoprene into, 1482.
Capillary constants of salts at their melting points, 7.
Capillary phenomena, application of, to the analysis of liquids, 236.
Caprylaldehyde, constitution of, 293.
Caproic acid, dibromo-, decomposition of, 960.
Capryl iodide, action of, on trimethylamine, 806.
Capsaicin, 1263.
Capsicum annuum, fruit of, 1263.
Carbamic acid, occurrence of, in horse's urine, 518.
Carbamide, action of phenylhydrazine on, 1323.
—— crystallisation of, by sublimation, 1309,
—— volatility of, 1309.
Carbamide. See also Urea.
Carbamido-acids, 827.
Carbaminethioacetophenone, 1317.
Carbamine-β-thiolactic acid, 440.
Carbanilidothiophenantialdoxime, 1435.
Carbanilidothiophensynaldoxime, 1435.
Carbaniltolylurethane, thio-, 600.
Carbazacridines, 617.
Carbazides, semithio-, bisubstituted, Trans., 1012.
Carbazole, 616, 1466.
—— amido-, 616.
—— behaviour of, towards carbonyl chloride, 167.
—— diamido, synthesis of, 480.
Carbin cyanide (methyl cyanide), 132.
Carbodiparatolylamide, stereoisomerism of, 1452.
Carbodiphenylimide, stereoisomerism of, 1452.
Carbohydrates, action of the bacillus of malignant œdema on, 91.
—— assimilation of, 742.
—— classification of the, 1066.
—— colour reactions of, 664.
—— estimation of, in vegetable products, 248.
—— influence of, on the accumulation of asparagine in plants, 91.
—— of putrefying human urine, 226.
—— production of acetic acid from 1421.
—— thermochemistry of, 763.
Carbon, action of, on sodium sulphate in presence of silica, 565.
—— action of, on sulphurous anhydride at high temperatures, 681.
—— allotropic states of, 405.
—— amorphous, allotropism of, 945.
—— and silica, action of, on chromic fluoride, 20.
—— and silicon, compounds of, 1050.
—— bisulphide, detection of in toxicological cases, 1520.
—— —— flame, experiments on, Trans., 216.

Carbon bisulphide, toxic action of, 1520.
—— bivalent, 1438.
—— chlorobromides, 771.
—— deposited from coal gas flames, Proc., **1892**, 46.
—— diiodide, 1291.
—— estimation of, in iron, 913, 1030.
—— examination of various forms of, 1273.
—— oxysulphide, preparation of, 15.
—— peculiar form of, 565.
Carbon-chains, closed, synthetical formation of, Trans., 36, 67.
Carbonic anhydride, absorption-coefficient of, in water and in alcohol, 1044.
—— —— atmospheric, estimation of, 533.
—— —— combined and free, apparatus for the estimation of, 531.
—— —— in the urine, 649.
—— —— influence of oxygen on the separation of, in the lungs, 1369.
—— —— new isothermal curves for, 3.
—— —— reactions of, at high pressures, 274.
—— —— supersaturated aqueous solutions of, 1274.
Carbonic anhydride-regenerator-gas, reconversion of heat into chemical energy by production of, 673.
Carbonic oxide, absorption coefficient of, in water, 1043.
—— —— absorption of, by the blood of a living mammifer, 743.
—— —— action of, on iron and manganese, 568.
—— —— and oxygen, influence of steam and other gases on the combustion of, 274.
—— —— detection of traces of, 99.
—— —— estimation of, 1128.
Carbonic-oxide-hæmoglobin, solutions of, Trans., 159.
Carbonylchloroplatinite, derivatives of, 352.
Carbonylphenyl-β-naphthylthiocarbamide, 984.
Carbonylphenylparatolylthiocarbamide, 984.
Carboparatoluidobenzantialdoxime, 1435.
Carboparatoluidobenzsynaldoxime, 1435.
Carboparatoluidofurfursynaldoxime, 1434.
Carborthotoluidothiophensynaldoxime, 1436.
Carbostyril, bromopseudochloro-, 630.
Carboxyantiglyoxime, 816.
Carboxy-α-hydroxycinnamic lactone, ortho-, 857.
Carboxyphenylglyceric acid, ortho-, δ-lactone of, 857.
Carboxypimelic acid, α-, 428.
Carboxysynglyoxime, 816.
Carnallite, extraction of rubidium and cæsium compounds from, 1395.
Carrots, cooked, composition of, Trans., 227.
Carvacrol, behaviour of, towards reducing agents, 157.
—— bromamido-, 595.
—— bromo-derivatives of, 156.
—— derivatives of, 309, 1312.
—— preparation of, 1311.
Carvene, constitution of, 1350.
Carvole, derivatives of, 499.
Cascarin, 1483.
Cassia, oil of, estimation of cinnamaldehyde in, 924.
Catechol in the urine of hydrophobic rabbits, 1115.
—— sodium derivatives of, 1184, 1185.
—— thermochemistry of, 764.
Cauliflower, cooked, composition of, Trans., 227.
Celery, cooked, composition of, Trans., 227.
Celestine from Scharfenberg, 1406.
Cell, Latimer Clark standard, practical form of, 669.
Cell. See also Battery, Galvanic Cell.
Cell-membranes, vegetable, 907.
Cellulose, 693.
—— benzoates, 693.
—— colloïdal solutions of, Trans., 156.
—— dissolving enzyme in the digestive tract of certain animals, search for a, Trans., 352.
—— estimation of, 923.
—— nitrates, action of alkaline solutions on, 692.
—— production of acetic acid from, 1421.
—— sulphite-, dextrose from, 801.
—— thermochemistry of, 764.
Cellulose-gum, 129.
Celluloses, 907.
Cereals, development of, 1119.
Cerium-earths, 1400.
Cerium-group, separation of the metals of, 686.
—— spectroscopic researches on, 686.
Cerotic acid, bromo-, 1302.
Cerous oxide, reaction for, 239.
Cetyldeoxybenzoïn, 1224.
Chabasite from the Faroe Islands, 1408.
Change, interval of, 1145.
Cheese, estimation of fat in, 392.
Chemical action at a distance, 268, 269.
—— phenomena, application of the second law of thermodynamics to, 3.
—— —— at very low temperatures, 1138.

Cherry laurel, occurrence of mannitol and sorbitol in the fruit of, 908.
Chestnut-wood tannin, 716.
Chloral, action of hydroxylamine on, 699.
—— bornylate, 228.
—— condensation of, with paraldehyde and ketones, 694.
—— menthylate, 228.
Chloralacetone, 694.
Chloralacetophenone, 695.
Chloralaldol, 695.
Chloraldoxime, 33.
Chloralhydroxylamine, 699.
Chloralimide, 134.
—— dimolecular, 134.
—— trimolecular, 134.
Chloranilic acid, action of halogens on, 834.
—— —— and bromanilic acid, compound of, Trans., 574.
—— —— crystallography of the sodium salt of, Trans., 583.
Chlorates, iodometric estimation of chloric acid in, Trans., 87.
Chlor-α-dibromhydrin, action of zinc-dust and alcohol on, 1293.
Chloric acid, estimation of, 236.
—— —— iodometric estimation of, in chlorates, Trans., 87.
—— —— volumetric estimation of, 1375.
Chlorides, estimation of, 527.
—— metallic, action of magnesium on, 777.
—— —— physical properties of solutions of, Trans., 339.
Chlorine, active, in bleaching powder, estimation of, 1374.
—— and bromine, detection of, in presence of iodine, 1514.
—— —— relative orienting effect of, Proc., **1892** 40.
—— and oxygen, reaction of, with hydrogen, 1147.
—— bromine, and iodine, exchange of, between inorganic and organic haloïd compounds, 574.
—— —— —— separation of, 1028.
—— direct combination of, with metals, 118, 401.
—— measurement of light intensity by the expansion of, 253.
—— separation of, from mercury and phosphoric and arsenic acids, 530.
—— use of platinous chloride as a source of, Trans., 445.
Chlorite, manganiferous, from Harstigen Mine, Sweden, 1411.
Chlorite-group, theories of the structure of, 794.
Chlorites, constitution of, 125.
Chloritoïd from Michigan, 793.
Chlorocruorin, 1256.
Chloroform, action of alkali sulphides on, 421.
—— impure, physiological action of, 744.
—— peculiar phenomena in the solidification of, 1138.
Chlorophyll, 1355.
—— crystals of, 1356.
—— influence of phosphoric acid on the formation of, 1261, 1272.
—— substances accompanying, in leaves, 746.
Chlorophyllane, nature of, 1136.
Chlorophyllic extracts, analysis of, 1136.
—— substances of the pericarp of the grape, 874.
Chlorosis, treatment of, with hydrochloric acid, 1117.
Cholesterol, estimation of, 248, 544.
—— vegetable, 1294.
Cholic acid, 741.
Choline, action of hydriodic and hydrobromic acids on, 808.
—— and neurine, relations between, 219.
—— derivatives of, 806, 905.
—— in cotton-seed foods, 380.
Chromammonium salts, 782.
Chromates, volumetric estimation of, 1375.
Chrome-iron-ore, analysis of, 1031.
—— decomposition of, 240.
Chrome-tourmaline from Maryland, 1057.
Chrome-yellows, analysis of, 663.
Chromic acid, Trans., 405.
—— —— estimation of, 103, 538.
—— anhydride, action of sulphur on, 770.
—— chloride, solutions of, Trans., 153.
—— hydrate, colloïdal solution of, Trans., 154.
—— hydrogen potassium pyrophosphate, 1053.
—— oxide, estimation of, 104.
—— sulphate, green, 411.
—— —— isomeric forms of, 411.
Chromite, analysis of, 1525.
Chromium ammonium thiocyanate, derivatives of, 798.
—— estimation of, in chromium-aluminium alloys, 1131.
—— estimation of, in steel, 538.
—— metallic, attempts to prepare, from chromic fluoride, 19.
—— salts, action of heat on solutions of, 571.
—— test for, 1133.
Chromium-bases, constitution of, 783.

Chromosulphuric acid and its salts, 783.
Chrysaniline, action of methyl iodide and hydroxide on, 1095.
—— azo- and alkyl compounds of, and the dyes therefrom, 1095.
Chrysanthemine, 84.
Chrysanthemum cinerariæfolium, constituents of the buds of, 349.
—— flowers, new alkaloïd from, 84.
Chrysidines, *α*- and *β*-, and their derivatives, 198.
Chrysophanic acid, 1354.
Cicuta maculata, examination of, 232.
Cincholine, 1492.
Cinchona alkaloïds, 1249.
—— —— alkyl derivatives of, 1012.
—— —— compounds of, with hydriodic acid, 83.
—— —— halogen derivatives of, 1010.
—— —— hydriodo-compounds of, 1363.
—— —— sulphonic acids of, 514.
Cinchonic acid, alkyl and alkylene derivatives of, 1488.
—— —— ethiodide, 1490.
—— —— ethobromide and ethochloride, 1489.
—— —— ethylbetaïne, 1490.
—— —— methobromide, methochloride, and methiodide, 1489.
—— —— methylbetaïne, 1489.
—— —— propobromide, 1491.
Cinchonidine benzyl salts, 1251.
—— compounds of, with hydriodic acid, 83.
—— ethiodides and methiodides, 1251.
Cinchonidinesulphonic acid, 515.
Cinchonine, 892.
—— action of hydriodic acid on, 514, 639.
—— chloride, 1011.
—— —— hydrochloro-, 1011.
—— compounds of, with hydriodic acid, 83.
—— dichloro-, 1011.
—— diethyl salts, 1252.
—— ethocyanide, 1251.
—— hydriodo-, salts of, 1363.
Cinchoxinic acid, alkylene derivatives of, 1488.
Cineolic acid, 1480.
—— —— constitution of, 866.
—— allylamide, 1480.
—— diethylamide, 1480.
—— paratoluidide, 1480.
—— phenylhydrazide, 1480.
—— piperidide, 1480.
Cinnamaldehyde, estimation of, in oil of cassia, 924.
Cinnamdiureïde, 57.
Cinnamene, condensation of, with phenols, 446.
Cinnamene, triiodo-, 470.
Cinnamenyloxazoline, *μ*-, 215.
Cinnamenylpentoxazoline, *μ*-, 215.
Cinnamic acid, condensation of, with hydrocarbons, 1228.
—— —— condensation of, with phenols, 848.
—— —— *β*-dibromo-, 1464.
—— —— *αβ*-dichloro-, 1464.
—— —— diiodo-, 470.
—— —— oxidation of, 986.
—— —— refractive power of, at different temperatures, Trans., 306.
—— acids, isomeric *α*-bromo-, Trans., 278.
—— —— stereoisomeric and polymeric, 469.
—— diphenylhydrazide, 981.
Cinnamon, oil of, 1509.
Cinnamylideneorthamidophenol, 1452.
Cinnamylideneparamidophenol, 1451.
Cinnamylphenylazimide, formation of, Trans., 282.
—— imide of, Trans., 283.
—— reduction of, Trans., 284.
Cinnamyltetrahydroketonaphthaquinoxaline, 886.
Cinnamyltetrahydroketoquinoxaline, 886.
Cinnoline, chloro-, 1494.
—— derivatives of, 1494.
Citraconic acid, conversion of, into its isomerides by soda, 297.
Citrates, alkali, 149.
Citrazinic acid, Trans., 1008.
Citric acid, 824.
—— —— anhydro-derivatives of, Trans., 1003.
—— —— detection of tartaric acid in, 546.
—— —— dissociation constant of, Trans., 708.
—— —— separation of malic acid from, 1531.
—— —— thermochemistry of, 763.
Citronellic aldehyde, 1068.
Citrus bergamia, stearoptene from the oil of, 71.
Clamps for gas analysis apparatus, 524.
Clay, chromiferous, from Brazil, 1057.
Clover, red, assimilation of free nitrogen by, 373, 374.
Cloves, oil of, valuation of, 250.
Coagulation and calcium salts, 1112.
—— of the blood, 87, 1112.
Coal, action of dilute nitric acid on, Proc., **1892**, 9.
—— formulæ for calculating the heating power of, 1143.
—— heats of combustion of products of the distillation of, 395.

Coal, valuation of, for use in steam boilers, 668.
Coal-dust explosions, lecture experiment to illustrate the phenomena of, TRANS., 414.
Coal-gas flames, carbon deposited from, PROC., **1892**, 46.
—— —— —— experiments on, TRANS., 205, 210.
—— —— —— formation of sulphuric acid in, 1374.
—— —— —— luminosity of, TRANS., 322.
—— —— formation of sulphuric acid and ammonium sulphate by burning, 1151, 1389.
Cobalt, action of nitric acid on, 1279.
—— action of nitric oxide on, 1152.
—— atomic weight of, 1159.
—— chloride, hydrates of, 569, 571.
—— —— vapour pressure of aqueous solutions of, 263.
—— —— variations in colour of, 569, 570.
—— detection of, 1525.
—— estimation of, in manganese ores, 917.
—— fluoride, 1160.
—— fluoroxyhypovanadate, 787.
—— mercuric thiocyanate, 10.
—— nitro-, 1390.
—— occlusion of hydrogen by, 567.
—— potassium fluoride, 782.
—— reactions of, 1132.
—— salts, action of alkaline polysulphides on, 537.
—— —— colour of solutions of, 278.
—— separation of iron from, 103.
—— separation of manganese from, 240.
—— sulphate, anhydrous, 941, 1283.
Cobalt-bases, constitution of, 783.
Cobra poison, 1118.
Cocaïne hydrogen diaminechromium-thiocyanate, 1001.
Coca leaves, Javan, alkaloïd from, 361.
Coco-nut fat, detection of, in butter, 391.
Codeïne, reactions of, 756.
Codeïne-violet, 360.
Coffee substitutes, analysis of, 1534.
Collidine, preparation of, 725.
Colloïd solutions, nature of, 766.
—— —— pedetic motions in relation to, PROC., **1892**, 17.
Colour and constitution of compounds, 561.
—— appearance of, in quinoline derivatives, TRANS., 789.
—— as an evidence of isodynamic change, PROC., **1892**, 103.
—— origin of, PROC., **1892**, 101, 103; TRANS., 789.
Colour-photometry, PROC., **1891**, 150.
Combustion, incomplete, analysis of the products of, 407.
—— of carbonic oxide and oxygen, influence of steam and other gases on, 274.
—— slow, of gaseous mixtures, 938.
Combustion-furnace, new, 1514.
Compounds, double, solubility of, 1047.
Compressibility and indices of refraction of liquids, relations between, 669.
—— of saline solutions, 766.
Concentration, effect of, on alcoholic fermentation, TRANS., 369.
Condensation and evaporation, spheres of, 1149.
Condenser, new, 400.
Conductivity. See Electrical Conductivity.
Condurangin, 1352.
Congo-red, colloïdal solutions of, TRANS., 156.
Constitution and colour, relation between, PROC., **1892**, 101, 103; TRANS., 789.
Contact, potential, differences of, 553.
Conyrine, oxidation of, 1104.
Copaiba, estimation of volatile oil in, 244.
Copiapite, 1408.
Copper, action of chlorine and of bromine on, 118.
—— action of nitric oxide on, 1152.
—— ammonium sulphate, 1399.
—— and cadmium, separation of, 534.
—— apparent variability of the electrochemical equivalent of, 105.
—— chloride, ammoniacal, action of potassium cyanide on, 1065.
—— —— measurement of the vapour pressures of solutions of, TRANS., 775.
—— —— solubility of, in various organic liquids, 558.
—— electrolytic detection of, 541.
—— electrolytic separation of mercury from, 239.
—— estimation of, by de Haen's (Brown's) method, 753.
—— estimation of, in aluminium, 1131.
—— formate, 140.
—— hydrosulphides, TRANS., 120.
—— lowering of the freezing point of bismuth by, TRANS., 893.
—— lowering of the freezing point of cadmium by, TRANS., 898.
—— lowering of the freezing point of lead by, TRANS., 905.
—— mercuric thiocyanate, 10.
—— nitrate, basic, decomposition of, by water, 1272.
—— nitride, supposed, 409.
—— nitro-, 1390.

Copper, nitrosonaphtholsulphonate, 346.
—— occlusion of hydrogen by, 567.
—— oxalate, 1431.
—— —— and pyridine, compound of, 1431.
—— oxide, anhydrous, 1399.
—— permolybdate, 1160.
—— phosphides, 410.
—— precipitation of, by iron, 276.
—— red, estimation of sulphur in, 753.
—— reduced, retention of hydrogen and carbon by, 942.
—— sulphate, basic, 1399.
—— —— crystallised anhydrous, 941, 1399.
—— —— solutions, dilute, cryoscopy of, 1045.
—— sulphite, basic, 1051.
—— sulphites, 1051.
Copper. See also Cuprous.
Copper-glance, oxidation of, by the electric current, 239.
Cordierite as contact mineral, 1056.
Corn-cockle, metabolism in pigs fed on, 1018.
Corycavine, 1367.
Corydaline, 1366; TRANS., 244, 605.
—— action of hydrogen iodide on, TRANS., 609.
—— allyl iodide, TRANS., 249.
—— ethyl sulphate, TRANS., 607.
—— hydriodide, TRANS., 246.
—— hydrobromide, TRANS., 607.
—— methiodide, TRANS., 248.
—— platinochloride, TRANS., 247.
Corydalis cava, alkaloïds of the root of, 1366.
—— *tuberosa*, alkaloïd from, TRANS., 244, 605.
Coto bark, constituents of, 60, 873.
Cotonoleïc acid, 584.
Cotton plant, chemical study of, 1510.
—— —— feeding value of, 1510.
Cotton-seed foods, choline and betaïne in, 380.
—— oil, constituents of, 584.
—— products, 584.
Coumarin, derivatives of, 988.
—— thio-, and its analogues, 329.
Coumarone, reduction of, 1318.
Cream, estimation of fat in, 392.
Creatinine, estimation of, in urine, 1135.
—— influence of muscular work on the elimination of, 364.
Cresyl orthacetates, meta-, ortho-, and para-, 308.
Crocoïte, synthesis of, 792.
Crops, assimilation of phosphoric acid by, 233.
—— leguminous, sources of the nitrogen of, 367.
Crotonaldehyde, action of sulphurous anhydride on, 424.
—— preparation of, 809, 1423, 1424.
Crotonaldoxime, 33, 580.
—— dichloro-, 34.
Crotonanilide, amido-, 965.
—— β-amido-, 708.
Crotonic acid, oxidation of, 957.
—— acids, bromo-, 961.
Crustaceæ, blue colouring matter of the blood of, 898.
Cryoscopic behaviour of dilute solutions, 8, 678, 1045.
—— determinations, 765.
Cryoscopy of cane-sugar solutions, 109, 678, 1046.
—— of dilute alcohol solutions, 1045.
—— of dilute calcium chloride solutions, 1045.
—— of dilute calcium nitrate solutions, 1045.
—— of dilute copper sulphate solutions, 1045.
—— of dilute ether solutions, 1045.
—— of dilute sodium chloride solutions, 1045.
—— of dilute urea solutions, 1045.
Cryptogams, assimilation of free nitrogen by, 370, 378.
Cryptopine and its derivatives, PROC., 1891, 166.
Crystallisation, water of, 581.
Crystals, artificial colouring of, 269.
—— influence of foreign substances on the form, purity, and size of, 937.
—— mixed, 1048.
—— —— formation of, 10.
—— —— solubility of, 265, 266, 560.
—— theory of the structure of, 572.
Cucumbers, cooked, composition of, TRANS., 227.
Cumarhydrin, para-, 873.
Cumenylacrylic acid, nitration of, 43.
Cumic acid, paradibromo-, 605.
Cumindiureïde, 57.
Cuminylanilide, 489.
Cumonitrile, propoxy-derivatives of, 595.
Cumylphosphinic acid, ψ-, 1035.
Cuprammonium acetobromide, 953.
—— oxalate, 1431.
—— oxide, 18.
Cupreïne, 1253.
—— behaviour of, with methyl iodide, 221, 892.
—— conversion of, into quinine, 1010.
Cuprodescloizite from Mexico, 1055.
Cuprous acetylide, 1416.
—— —— preparation of, 421.
—— iodide and ammonium thiosulphate, compounds of, 1157.
—— sulphite, 1052.

Current reversal, 759.
Curvature, the recognition of changes of, by means of a flexible lath, 767.
Cusparia trifoliata, constituents of, 642.
Cusparine, 643.
Cusparidine, 643.
Cyanacetophenone, action of hydroxylamine on, 324.
—— and its derivatives, 324, 845.
Cyanacetothienone, 304.
Cyanacetylaniline, 1072.
Cyanacetylbenzylamine, 1072.
Cyanides, condensation of, with ethereal salts, 431.
Cyanobenzoic acid, parabromometa-, 337.
Cyanobenzoylacetone, α-, 451.
Cyanocamphor, azo-derivatives of, 1343.
Cyanocarbamides, 702.
Cyanocinnamic acid, α-, 1087.
Cyanogen flame, experiments on, TRANS., 215.
Cyanomethæmoglobin, 361.
Cyanonitrometaxylene, 1437.
Cyanoparatolylformamidine, 707.
Cyanophenylformamidine, 707.
Cyanothiocarbamides, 702.
Cymene, oxidation of, 724.
—— synthesis of, 1310.
Cysteïn, 1111.
Cystin, 1111.
—— presence of, in the horse's liver, 526.

D.

Darapskite, 124.
Datura stramonium, alkaloïds of, 232.
Daturic acid, bromo-, 582.
—— —— salts of, 582.
Daturone, 582.
Decacetyldiglucoheptose, 1167.
Decamethylenediamine, 1181.
Decamethyleneimine, 1181.
Decyl acetate, bromo-, 691.
—— benzoate, chloro-, 691.
Decylacetylene, 1164.
Decylene and its derivatives, 691.
—— glycol, 691.
Dehydracetic acid, 584.
—— —— bromo-, 584.
—— —— constitution of, 587.
—— —— oxy-, 585.
—— —— preparation of, 296.
—— chloride, 587.
Dehydracetylpæonol, 846.
Dehydrocholic acid, 741.
—— —— chloro-, 741.
Dehydrocinchen dibromide, 1012.
Dehydrocinchonine dibromide, 1011.
Dehydrodiacetovanillone, 61.
Dehydrodiacetyllevulinic acid, action of ammonia on, 1429.
—— —— action of benzaldehyde on, 1429.
—— —— action of hydroxylamine and phenylhydrazine on, 1429.
—— hydrazone, 1429.
—— oxime, 1429.
Dehydrodiacetylpæonol, 845, 846.
Dehydrodiacetylresacetophenone, 846.
Dehydrodypnopinacolin, 995.
Dehydromethylacetylpæonol and its derivatives, 846.
Dehydronicotine, 1010.
—— dibromo-, 1497.
Dehydrothiotoluidine, synthesis of, 839.
Density, maximum, of water, 7.
—— molecular weight, diathermanous power, and refractive index of a substance, relation between, 1.
—— of liquefied gases and of their saturated vapours, determination of, 934, 1043.
Deoxybenzoïn, action of paramidodimethylaniline on, 855.
—— chloro- and diiodo-, 451.
—— derivatives of, 1227.
—— parachloro-, 1227.
—— paranitro-, 1227.
—— preparation of, 1095.
—— sodium derivative of, 171.
Deoxybenzoïns, 338.
Deoxyfulminuric acid, 1417.
Deoxystrychnic acid, 1014.
Deoxystrychnine, 1013.
Desaurin, 1095.
—— action of sulphuric acid and of aniline on, 1096.
—— parachloro-, 1227.
Desaurins, new method of formation of, 340.
Desiccator, new form of, 524.
Desmine- and heulandite-groups, relations between minerals of the, 417.
Desylacetic acid, 1002.
Dextran, thermochemistry of, 764.
Dextrin, action of alkaline mercuric cyanide on, 1032.
—— estimation of, in beer and beer wort, 248.
—— preparation of, 577.
Dextrins, fermentability of, 922.
Dextrose, action of alkaline mercuric cyanide on, 1032.
—— cane-sugar, and invert-sugar, examination of mixtures of, 248.
—— disappearance of the multirotation of, in ammoniacal solution, 1419.
—— estimation of, in beer and beer wort, 248.
—— estimation of, in vegetable products, 249.

Dextrose, fermentation of, with *Bacillus ethaceticus*, TRANS., 436.
—— from sulphite cellulose and from fir wood, 801.
—— obtained from cane sugar by means of invertase, specific rotatory power and cupric-reducing power of, TRANS., 408.
Dextrose. See also Glucose.
Dextrose-series, ascent of the, 1164.
Dextroso-cellulose, 907.
Diabase, products of the weathering of, 1412.
Diabetes, artificial production of, 364.
—— variations of glycolytic and saccharific powers of blood in, 517.
Diabetic, behaviour of milk sugar in a, 903.
Diacetallylthiocarbamide, 1327.
Diacetin, preparation of, 289.
Diacetodiketohexamethylenedicarboxylic acid, 586.
Diacetohydroxamic acid, 699.
Diacetonamine platinothiocyanate, 287.
Diacetophenonethylenediphenyldiamine, 633.
Diacetoxydiphenyl sulphoxide, 1077.
Diacetyl, preparation of, 425.
Diacetylacetone, TRANS., 825, 858.
—— chlorinated, 811.
—— refractive and dispersive powers of, TRANS., 860.
Diacetylamidoethenylamidocarvacrol, 309.
Diacetyl-1 : 4-amidonaphthol, 862.
Diacetylchloralammonia, trimolecular, 134.
Diacetyldiamidotoluene, dinitro-, 1197.
Diacetyldiamylquinol, 1444.
Diacetyldiisoeugenol, 46.
Diacetylglycerol, 288.
—— chloro-, 289.
Diacetylindigotin, 480.
Diacetylisoeuxanthone, 504.
Diacetylmetachlorobromoquinol, TRANS., 563.
Diacetylmetadichlorobromoquinone, TRANS., 567.
Diacetylmetadichlorodibromoquinol, TRANS., 580.
Diacetylmetadichloroquinone, TRANS., 560.
Diacetylmetapropenylcatechol, 973.
Diacetylmethylenediamine, 579.
Diacetylnitro-xylidine, 1437.
Diacetylorthodiamidotoluene, nitro-, 1197.
Diacetylorthodiamines, 1197.
Diacetylparadichlorobromoquinol, TRANS., 565.
Diacetylpiperazine, 211.
Diacetyl-β-resorcylonitrile, 317.
Diacetylrubbadin, 1076.
Diacetyltartaric acid, stereochemistry of, 669, 758, 759.
Diacetyltartaric-derivatives, rotatory power of, 669.
Diacetyltrichlorobromoquinol, TRANS., 593.
Diallylacetone, 435.
Diallylacetonedicarboxylic acid, 435.
Diallyldithiotetrahydrotriazole, 292.
Diaminechromium hydrogen thiocyanate, compounds of nitrogenous bases with, 1000.
Diamines in diseases, 518.
—— ortho-, 1472.
—— —— action of formaldehyde on, 1496.
—— —— and α-hydroxy acids, constitution of the compounds obtained from, 1359.
Diammonium imidosulphonate, TRANS., 946.
Diamond, artificial corrosion of, 1394.
—— specific heat of, 761.
Diamonds, discovery of, in meteoric iron, 284.
Diamylamine, chloro-, action of sodium and potassium cyanide on, 804.
Diamylcatechol, 1445.
Diamylcyanamide, 804.
Diamylpyrogallol, 1445.
Diamylquinol, 1443.
—— phenylcarbamate, 1444.
Diamylquinone, 1444.
Diamylresorcinol, 1444.
Dianildicyandiamide, 1323.
Dianilidobenzene, para-, derivatives of, 1450.
Dianilidodimetanitrobenzophenone, para-, 336.
Dianilidosuccininanilide, acetyl derivatives of, 55.
Dianisylditrosacyl, 971.
Diapocinchonine, 1253.
Diargentic sodium imidosulphonate, TRANS., 975.
Diarrhœa, sulphates and ethereal hydrogen sulphates in urine during, 1505.
Diastase, 92.
Diastatic action, TRANS., 689.
Diathermanous power, refractive index, density, and molecular weight of a substance, relation between, 1.
Diazinedicarboxylic acid, 507.
Diazoamidobenzene, action of paratoluidine on, 978.
—— meta- and para-dichloro-, action of paratoluidine on, 978.
Diazoamido-compounds, 977.
—— —— action of acetic anhydride on, 458.

Diazoamido-compounds, action of aniline hydrochloride on, 979.
—— —— conversion of, into azoamido-compounds, 977.
—— —— ethylene derivatives of, Proc., 1892, 119.
Diazoamido-ψ-cumene, action of paratoluidine on, 978.
Diazoamido-ψ-cumeneparatoluene, 979.
Diazoamidometachlorobenzeneparatoluene, 979.
Diazoamidoparachlorobenzeneparatoluene, 979.
Diazoamidotoluene, ortho-, 459.
Diazobenzaldehyde, ortho-, 1106.
Diazobenzene, action of, on acetonedicarboxylic acid, 161.
—— chloride, action of benzaldoxime on, 163.
—— —— action of hydroxylamine on, 710.
—— perbromide, 316.
Diazobenzenamidocarbazole, 617.
Diazobenzeneglyoxaline, 1493.
Diazobenzene-β-naphthylamine, action of dimethylaniline on, 980.
Diazobenzenepiperazine, 211.
Diazo-compounds, action of oximes on, 163, 1079.
—— —— new synthesis by means of, 1198.
—— —— velocity of decomposition of, by water, 768.
Diazodibenzylamine, ortho-, 890.
Diazoguanidine salts, 1298.
Diazohippurylamide, 113.
Diazonaphthalene salts, nitro-, decomposition of, with alcohol, 622.
Diazonaphtholsulphonic acid, 721.
Diazonaphthylenesulphonic acid [1 : 2], 345.
Diazotoluene chloride, para-, action of hydroxylamine on, 710.
Dibenzamide, imido-, 713.
Dibenzenesulphonediphenetidine, 65.
Dibenzenesulphoneorthotoluylenediamine, 66.
Dibenzenesulphoneparaphenylenediamine, 65.
Dibenzenylazosulphime, 1109.
Dibenzimidine, 1110.
Dibenzoyldihydroxyanhydroecgonine, derivatives of, 1016.
Dibenzoyldiisoeugenol, 46.
Dibenzoyldiorthohydroxystilbene, 168.
Dibenzoylorthohomosalicenylamidoxime, 320.
Dibenzoylparahomosalicenylamidoxime, 319.
Dibenzoylpyridine, 1365.
Dibenzoylstilbene, action of phenylhydrazine on, 995.
Dibenzyl ketone, 851.
Dibenzylacetoacetic acid, 963.
Dibenzylamidosulphonic acid, 476.
Dibenzylamine nitrate, 476.
—— paradinitrorthodichloro-, 445.
Dibenzylaniline, paradinitrorthodichloro-, 445.
Dibenzylcarbamic chloride, 1083.
Dibenzylcarbinamine, 1093.
—— dibenzylcarbinaminethiocarbamate, 1094.
Dibenzylcarbinol, 851, 1094.
Dibenzylcyanocarbamide argentocyanide, 1084.
Dibenzyldiphenylsuccinonitrile, symmetrical, 619.
Dibenzylditolylcarbamide, 1083.
Dibenzylene dicyanide, 619.
Dibenzylidene-2 : 6-lutidine, 1361.
Dibenzylidenenitrotolidine, 852.
Dibenzylideneparadiamidodiphenylmethane, 618.
Dibenzylorthodiamidotoluene, nitro-, 1197.
Dibenzylparatolylcarbamide, 1083.
Dibenzylphenylhydrazine, diorthonitro-, 1456.
Dibenzylpimelic acid, ωω′-, dissociation constant of, Trans., 702.
Dibenzylpyridine, 1364.
Dibenzylsulphonemethane, 612.
Dibenzylsulphonephenylmethane, 623.
Dibenzylsulphonethiobenzylmethane, 612.
Dibornylamine, 1238.
Dibornylthiocarbamide, 1238.
Dicalcium phosphate, crystallisation of, 407.
—— —— solubility of, in solutions of phosphoric acid, 684.
Dicampholylcarbamide, 1345.
Dicarboxyglutaconic acid, Trans., 791.
Dichlorhydrin metahydroxybenzoate, an isomeric, 471.
Dicresol, 1467.
—— nitro-, 852.
Dicresoldisulphonic acid, 1467.
Dicyanacetylethylenediamine, 1071.
Dicyanacetylpentamethylenediamine, 1071.
Dicyanonaphthalene [1 : 2], 1477.
Dicyanophenylhydrazine, action of ethyl acetoacetate on, 597.
—— condensation of, with fatty aldehydes, 596.
Dicyanostilbene, 618.
Didymium spectra, 686.
Dielectric power and electrolytic conductivity, coexistence of, 759.
Diethoxydiamidodiphenylamine, 314.
Diethoxydimethyldiamidophenazine, 315.

Diethoxydiphenylcarbamide, 833.
Diethoxydiphenylenedinitrosacyl, para-, 972.
Diethoxysulphophenylhydrazide, para-, 1082.
Diethyl camphorate, 500, 1102.
—— dichlorobenzoparadifurfuran-α-dimethyl-β-dicarboxylate, para-, 609.
—— diphenylazimethylenedicarboxylate, 453.
—— furfuryllutidinedicarboxylate and its salts, 1362.
—— hydrofurfuryllutidinedicarboxylate, 1362.
—— isocamphorate, 501.
—— malonate, action of methylene iodide on, 1304.
—— quinoneparadifurfuran-α-dimethyl-β-dicarboxylate hydrochloride, 610.
—— sulphoxide, diamido-, picrate of, 130.
Diethylamidocaproic acid, 294.
Diethylamidophenylarsine oxide, 1321.
Diethylamine platinothiocyanate, 286.
Diethylaniline, action of silicon tetrachloride on, Trans., 457.
Diethylcamphor, 200.
Diethyldiamidoquinoxazone, 888.
Diethyldithiophosphinic acid, 1422.
Diethylethoxydiphenylsulphonephenylenediamine, 161.
Diethylidenecinchonine, 1252.
Diethylidenecinchoxine, 1252.
Diethylorthotoluidine, paramido-, 1078.
Diethylpentanetetracarboxylic acid, dissociation constant of, Trans., 704.
Diethylphenylformamidine, 707.
Diethylpimelic acid, $\omega\omega'$-, dissociation constant of, Trans., 701.
Diethylpiperazine, 212.
Diethylpiperidine, 1358.
Diethylpropargylamine hydriodide, 30.
Diethylquinol, trinitro-, action of dimethylmetadiamidobenzene and of α-naphthylamine on, 315.
—— —— action of dimethylparamidobenzene on, 315.
—— —— action of paradiamidobenzene on, 314.
Diethylsulphonephenylsulphonemethane, and its chloro- and bromo-derivatives, 613.
Diethylsulphonephenylsulphonemethylmethane, 613.
Diethylsulphonethiophenylmethylmethane, 613.
Diethylthiocarbamide, unsymmetrical, 216.
Diethyltoluylenediamine, 66.
Difenchyloxamide, 1239.
Difenchylthiocarbamide, 1239.
Diffusion and electrolysis, theory of, 935.
—— of aqueous solutions, 1265.
Diformylparadianilidobenzene, 1451.
Difurfurylcarbamide, 43.
Difurfurylthiocarbamide, 43.
Difurylhydroxycyanidine, 1008.
Difurylmethylcyanidine, 1006.
Difurylnaphthoquinoxaline, 1475.
Difurylquinoxaline, 1475.
Difuryltoluquinoxaline, 1475.
Digestibility of raw and boiled meat, 1367.
Digestion and absorption of fat oils by plants, 1118.
—— gastric, influence of amido-acids on, 742.
—— of carbohydates, 742.
—— of pentose carbohydrates, 645.
—— of starch by dogs, 516.
—— peptic, influence of wine on, 87.
Digestive ferments in crustacean eggs, 362.
—— tract of certain animals, search for a cellulose-dissolving enzyme in, Trans., 352.
Digitaleïne, 222.
Digitaligenin, 1482.
Digitalin, 1482.
Digitalonic acid, 1241.
—— lactone, 1242, 1482.
Digitalose, 1482.
Digitogenin, preparation of, 1483.
Digitonin, 501.
Dihydrazidopimelic anhydride, 435.
Dihydrazineditolyldisulphonic acid, 1467.
Dihydriodoapoquinidine, 640.
Dihydriodocinchonine, 514, 639.
Dihydriodoquinidine, 640.
Dihydroarecaïdine, 739.
Didydroarecoline, 739.
Dihydrobenzene, synthesis of, 1074.
Dihydrobenzyldimethylamine, $\Delta^{3:5}$-, 358.
Dihydrocarveol, 499.
Dihydrocarvylamine, 499.
Dihydrodimethylnaphthylpropionic acid, 871.
Dihydroisosantinic acid, 871.
Dihydro-α-naphthoic acid, labile Δ^{2}-, 192.
—— —— stable Δ^{1}-, 192.
Dihydro-β-naphthoic acid, labile Δ^{3}-, 193.
—— —— stable Δ^{2}-, 193.
Dihydroparaxylene, synthesis of, 1182.
Dihydrophenanthridine, 197.
Dihydrophthalic acid, $\Delta^{1:4}$-, 1216.
—— —— $\Delta^{4:6}$-, 1215.
—— —— cis-$\Delta^{3:5}$-, 1215.
—— —— trans-$\Delta^{3:5}$-, 1214.

Dihydroquinazoline, 219.
Dihydrosantinic acid, 871.
Dihydroterephthalic acid, nitrile of, 834.
Dihydrotrimethylindolé methiodide, 614.
Dihydroximidopropionic acid, primary, 815.
—— —— secondary, 816.
Dihydroxyacridine, 1108.
Dihydroxyaldehydes, aromatic, nitrogenous derivatives of, 317.
Dihydroxyamylpiperidine aurochloride, 86.
Dihydroxyanhydroecgonine, 1015.
Dihydroxyanisoïl, dinitro-, 596.
Dihydroxyaurindicarboxylic acid, 1469.
Dihydroxybenzoic acid, 1 : 3 : 5-, action of chlorine on, 1461.
—— —— dichloro-, 1461.
—— —— trichloro-, 1461.
Dihydroxybutyric acid, 957.
Dihydroxycaproic acid, salts of, 959.
Dihydroxy-compounds, aromatic ortho-, reagent for, 1133.
Dihydroxydiketotetrahydronaphthalene, 859.
Dihydroxydinitrodiphenylamine, 310.
Dihydroxydiphenyl sulphoxide, 1077.
Dihydroxydiphenyldibenzylmethane, 851.
Dihydroxyfluoran, 970.
Dihydroxyhexamethylene, cistranspara-, 833.
Dihydroxyhydrobenzoïn, ortho-, 168.
—— —— diesoanhydride, 168.
Dihydroxyhydrolapachol, Trans., 647.
Dihydroxy-α-naphthaldehyde, β-ortho-1459.
Dihydroxynaphthaquinone, 720.
Dihydroxy-β-naphthaquinone, 494.
Dihydroxynaphtho-xanthones, 1100.
Dihydroxyorthocarboxyphenylpropionic acid, lactone of, 720.
Dihydroxyperchloromethylcyanidine, 1291.
Dihydroxy-α-picoline, α′γ-, Trans., 723.
—— dibromide, Trans., 724.
Dihydroxystilbene, ortho-, 168.
Dihydroxytartaric acid, behaviour of, with sodium hydrogen sulphite, 148.
Dihydroxythiobenzenes, 1316.
Dihydroxythymoquinone, 1098.
Dihydroxytoluene, synthesis of the sixth, 447.
Dihydroxytriphenylmethane, meta-, paranitro-, 621.
—— para-, metanitro-, 620.
—— —— orthonitro-, 621.
—— —— paranitro-, 621.
Dihydroxytriphenylmethanedicarboxylic acid, ortho-, para-, and meta-nitro-, 621.
Dihydroxyvaleric acid, salts of, 959.
Dihydroxyxanthone, bromo-derivatives of, 1226.
Diimide, attempts to prepare, 1430.
Diisoamylselenocarbamide, 216.
Diisoamylthiocarbamide, unsymmetrical, 216.
Diisobutylallylamine, 31.
Diisobutylamine, chloro-, 1173.
Diisobutylcyanamide, 1173.
Diisoeugenol and its derivatives, 45.
Diisopropylpimelic acid, ωω′-, dissociation constant of, Trans., 702.
Diketohexene, meta-, hexachloro-, 1461.
—— para-, hexachloro-, 447.
—— —— pentachloramido-, 450.
Diketohydronaphthalene hydrate, dichloronitro-αβ-, 1232.
—— tetrachlorortho-, its hydrates and alcoholates, 858.
Diketo-γ_1-methyljulole, $\alpha_1\alpha_2$-, 496.
Diketones, action of bleaching powder and of hypochlorous acid on, 720.
—— fatty 1 : 2-, preparation of, 425.
Diketopentamethylenehydroxycarboxylic acid, tetrachloro-, 836.
—— —— trichloro-, 835.
Dimethoxystilbene, ortho-, 719.
—— para-, 719.
Dimethyl camphorate, 1102; Trans., 1092.
Dimethylacetobutylamine, 1244.
Dimethyladipic acids, stereoisomeric, 430.
Dimethylalloxanhydrazone, 442.
Dimethylamidoazobenzene, parabromo-, 980.
Dimethylamidocrotonanilide, β-, 708.
Dimethylamidophenylarsine oxide, 1321.
—— sulphide, 1321.
Dimethylamidopropionic acid, 1302.
Dimethylamidoquinoxazone, 888.
Dimethylamine hydrogen diaminechromium thiocyanate, 1000.
—— platinothiocyanate, 286.
Dimethylaniline, action of, on ketones, 855.
—— refractive power of, at different temperatures, Trans., 302.
Dimethylapionylcarboxylic acid, 1315.
Dimethylbenzimidazole [2 : 2′-], 632.
Dimethylcinchonine, 892.
Dimethylcyanidine, amido-, 1291.
Dimethyldiamidodiphenyltolylmethane, paranitro-, 189.
Dimethyldiamidoquinoxazone, 888.
Dimethyldiazine, 507, 633.
Dimethyldihydropentene methyl ketone, Trans., 77.
—— —— ketoxime, Trans., 79.
Dimethyldihydropentenedicarboxylic acid, Trans., 81.

Dimethyldihydroquinazoline, βγ-, 218.
Dimethydihydroxyglutaric acid, 437.
—— —— dilactone of, 437.
—— —— lactone of, 436.
—— acids, stereoisomerism of, 436.
Dimethyldiketohexamethylene, 1183.
Dimethdiphenylsuccinonitrile, symmetrical, 619.
Dimethyldipiperidyl, 1487.
Dimethyldipyridyl, ββ-, 629.
Dimethyldiquinoyline, 1107.
Dimethyldisalicylaldehyde, para-, 1459.
Dimethyldithiotetrahydrotriazole, 293.
Dimethylethylnaphthalene, 872.
Dimethylethylsulphine, preparation of, 1422.
Dimethylethylthymoquinol, 1312.
Dimethylfraxetin, 628.
Dimethylglyceric acid, αβ-, from angelic acid, 297.
Dimethylheptylethylene, α-, 133.
Dimethylhexylcarbinol, 133.
Dimethylhydroxybutyrolactonecarboxylic acid, 436.
Dimethylhydroxyquinoline, 78.
Dimethylisoxazole, αγ-, reduction of, 507.
Dimethylmetamidophenol, nitroso-, 887.
Dimethyl-α-methoxy-μ-thiomethylimidazole, νβ-, 153.
Dimethylmethylenehydrazine, 457.
Dimethylmethyleneimidosulphonic acid, 701.
Dimethylnaphthalloxazine, 70.
Dimethylnaphthylpropionic acid, 871.
Dimethylorthanisidine, action of nitric acid on, 159.
Dimethylparethoxyphenylpyrazolone, 1080.
Dimethylpentamethylenemethylcarbinol, Trans., 79.
Dimethylpentanetetracarboxylic acid, dissociation constant of, Trans., 704.
Dimethylphenylcyanidine, 1110.
Dimethylphthalic acid, para-, 872.
Dimethylpimelic acid, ωω′-, dissociation constant of, Trans., 701.
—— acids, stereoisomeric, 430.
Dimethylpiperazine, 212.
Dimethylquinoline, αβ-, 1107.
—— amido-, 729.
—— nitro-, 729.
Dimethylquinolone, 4-nitro-, 880.
Dimethylquinitol, 1183.
Dimethylracemic acid, 698.
Dimethylrubbadin, 1077.
Dimethyltetrahydroquinoline, 614.
Dimethyl-Δ²-tetrahydropyridine, 1 : 2-, 1243.
Dimethylthetincarboxylic acid, 1433.
Dimethylthetindicarboxylic acid, 1433.
Dimethylthiocarbamide, unsymmetrical, 216.
Dimethylthiohydantoïn, 151.
Dimethyltoluidine, ortho-, action of formaldehyde on, 1320.
Dimethyltriamidodiphenylamine, 1109.
Dimethyltriamidodiphenyltolylmethane, 189.
Dimethyltrihydroxybenzophenone, 1225.
Dimethyltrimethylenedisulphone sulphide, 593.
Dimethyltrimethylenetrisulphone, 591, 593.
Dimethylumbelliferonecarboxylic acid, αβ-, 432.
Dimethylxanthone, 1093.
Dinaphthenylimidine, β-, 1110.
Dinaphtho-xanthone, 1099.
Dinaphthylamidinecarbamide, 1008.
Di-β-naphthylcarbamic chloride, thio-, 165.
Dinaphthylcarbamide, tetranitro-α-, 467.
—— tetranitro-β-, 467.
Di-β-naphthylcarbamide, unsymmetrical, thio-, 165.
Dinaphthyl-αγ-diketopiperazine, β-, 1342.
Dinaphthyl-αγ-dimethyl-βδ-diketopiperazine, β-, 1337.
Di-α-naphthylformamidine, 706.
Dinaphthylmethylcyanidine, 1110.
Di-β-naphthylphenylcarbamide, thio-, 166.
Dinaphthylthiocarbazide, β-, 513.
Dinaphthylthiocarbazone, β-, 513.
Dinitrosacyls, 971.
Dioxydehydronicotine, dibromo-, 1497.
Dioxymethylenephenyloximidoacetic acid, 327.
Dioxythiophenetoïl, 1316.
Dipentene, dihydrochloro-, action of chlorine on, 1350.
Dipentenenitrolanilide, α-nitroso-, 1348.
Dipentenenitrolbenzylamine, hydrochloro-, 1349.
Diphenyl, dimetanitrodiorthamido-, 481.
Diphenylacetonitrile, 344, 1094.
Diphenylamine, action of silicon tetrachloride on, Trans., 454.
—— diamido-, 1109.
—— formation of, from orthobromobenzoic acid, 1188.
Diphenylamineorthoparadisulphonic acid, 333.
Diphenylanthracene dibromide, 720.
—— dihydride, 720.
Diphenylcarbamide, bromo-, 833.
—— metachloro- and parachloro-, 979.
—— unsymmetrical thio-, 164.
Diphenylcrotolactone, 1002.
Diphenylcyanamide, Proc., 1892, 96.

Diphenyl-derivatives, dehydration of amides in contact with, 617.
Diphenyldiamidodicarboxylic acid, 1464.
Diphenyldi-β-naphthylcarbamide, symmetrical, 166.
—— thio-, 165.
—— unsymmetrical, 167.
Diphenylene oxide, synthesis of, 1470.
Diphenyleneazone, 184, 482.
—— diamido-, 184.
—— dioxide, 183.
—— oxide, 183.
Diphenylenediamine, para-, 481.
Diphenylenehydrazone, 184.
Diphenylformamidine, metadinitro-, 706.
—— metanitro-, 707.
Diphenylfurfurylguanidine, 43.
Diphenylhydantoïn, 1334.
Diphenylhydrazoneopianic acid, 1210.
Diphenylmaleïc acid, action of soda on, 297.
—— anhydride, 178.
Diphenylmethane, paradiamido-, 618.
—— —— nitro-derivatives of, 618.
Diphenylmethyleneaniline, 1195.
Diphenylmethylethophenazonium hydroxide, 1108.
Diphenylnitrosamine, orthonitro-, 332.
Diphenylorthamide, preparation of, 1198.
Diphenylpropionic acid, 849.
—— —— preparation of, 1228.
Diphenylpyrrolidone, 1003.
Diphenylpyrrolone, 1003.
Diphenylquinol, nitro-derivatives of, 310.
Diphenylresorcinol, tetra-, penta-, and hexa-nitro-, 310.
Diphenylsuccinonitriles, α- and β-, 619, 620.
—— stereoisomeric, 619.
Diphenyltetraketone, 69.
Diphenylthiazolecarboxylthiamide, 638.
Diphenylthiocarbamide, 600.
Diphenylthiohydantoïn, 468.
Diphenylthiourea, unsymmetrical, Proc., 1892, 96.
Diphthalimidoethyl sulphide, 130.
—— sulphoxide, 130.
Diphthalimidoethylsulphone, 131.
Diphtheria, chemical pathology of, 744.
Dipiperazine, paradinitro-, 210.
Dipiperidyl, 2 : 3-, 1365.
Dipotassium imidosulphonate, Trans., 952.
Dipropargyl and benzene, 1436.
—— constitution of, 1437.
—— molecular refraction of, 1437.
Dipropylcarbamide, unsymmetrical, 1421.
Dipropylpimelic acid, ωω′-, dissociation constant of, Trans., 701.
Dipropyltrimethylenetrisulphone, 592.
Dipseudocumylcarbamide, 832.
Dipyridyl carbonyl bromoplatinosite, 353.
—— —— chloroplatinosite, 352.
Dipyridyl-aa-dicarboxylic acid, 75.
Disanhydrotetrabenzamidotetrahydroxyoctene, 1002.
Disazobenzene, chloronitro- and chloronitronitroso-derivatives of, 456.
—— nitronitroso-derivatives of, 455.
Disazobenzenephenylhydrazine, pentanitro-, 456.
Disbenzeneazoacetine, 161.
Diseases, diamines in, 518.
—— infectious, ptomaïnes of, 1258.
Disodium imidosulphonate, Trans., 954.
Dispersion and refraction of sodium chlorate, 1.
Dissociation constants of organic acids, Trans., 696.
—— —— of stereoisomeric nitrogen compounds, 1268.
—— electrolytic, and absorbent power of coloured salts, 757.
—— —— and osmotic pressure, theories of, 1143.
—— —— of salts, determination of, by means of solubility experiments, 1143.
—— hypothesis and strong solutions, 108.
—— in dilute solutions of tartrates, 588, 1144.
—— of bismuth chloride by water, effect of sodium chloride on the, 122.
—— of electrolytes, correction in the calculation of the heat of, 931.
—— of liquid nitrogen peroxide, Trans., 242.
—— of phosphonium bromide, 401.
Dissolution, abnormal, 1047.
—— behaviour of molecular compounds on, 1154.
—— change of volume on, 264.
Dissymmetry, molecular, 399.
Disuccinimidodihydroxamic acid, 138.
Disulphanilic acid, 333.
Disulphones, formation of trisulphones from, 613, 850.
Ditetramethylene diphenyl glycol, Trans., 66.
Dithiocarbamates, aromatic, 55.
Dithiocarbonic acids, 306.
Ditolenylimidine, 1110.
Ditoluamide, para- and ortho-, 712.
Ditolyl ketone, diamido-, 1460.
—— —— dinitro-, 1460.
—— meta-, 851, 852.

Ditolyl dicyanide, meta-, 852.
Ditolylamine, orthamido-, derivatives of, 853.
—— orthamido-, formation of an, from parahydrazotoluene, 853.
Ditolylbenzylcarbamide, para-, 1083.
Ditolylcarbamic chloride, para-, 1083.
Ditolylcarbamide, meta-, 832.
Ditolylcarbazide, para-, 512.
Ditolylcyanocarbamide, diargentocyanide, para-, 1084.
Ditolyldicarboxylic acid, 852.
Ditolyl-$\alpha\gamma$-diethyl-$\beta\delta$-diketopiperazines, para-, 1338.
Ditolyl-$\alpha\gamma$-diketopiperazine, ortho-, 1334.
—— para-, 1337.
Ditolyl-$\alpha\delta$-diketopiperazine, para-, 1336.
Ditolyldisulphonic acid, 1466.
—— —— amido-, 1467.
Ditolylhydantoïn, ortho-, 1334.
—— para-, 1336.
Ditolylhydroxycyanidine, 1008.
Ditolylmethylcyanidine, 1110.
Ditolylsemithiocarbazide, ortho-, TRANS., 1017.
—— para-, TRANS., 1018.
Ditolylthiocarbazide, ortho-, 513.
—— para-, 512.
Ditolylthiocarbazone, ortho-, 513.
—— para-, 512.
Divalolactone, 814.
Dixanthone, 1097.
Dixylylcarbamide, 832.
Dogs, digestion of starch by, 516.
Dopplerite, 689.
Double salts, solubility of, 1145.
Dulcitol, a pure fermentation of, TRANS., 254.
—— and calcium chloride, compound of, TRANS., 275.
—— and its derivatives, optical properties of, 1419.
—— thermochemistry of, 764.
Duodecylacetylene, 1164.
Durene, chloro-, action of sulphuric acid on, 968.
—— iodo-, 967.
—— mono- and di-chloro-, 967.
Durenesulphonic acid, chloro-, 1465.
Dyeing with aniline black in the dry way, 323.
Dyes of the triphenylmethane group, 187.
Dypnopinacolene, 994.
Dypnopinacolin, α-, 993.
—— alcohol, 994.
Dypnopinacolin, β-, 994.
Dypnopinacone, 993.

E.

Earth-nut cake and meal, approximate estimation of adulteration of, 1535.
—— meal, 92.
Earths of the cerium and yttrium 1400.
Ecgonine, constitution of, 360.
Effusion of gases, lecture experiment on, 1150.
Egg yolk, estimation of fat in, 1134.
Eggs, crustacean, digestive ferment in, 364.
Elaïdic and oleïc acids, stereoisomerism of, 812.
Ellagic acid, 990.
Elaterite, 689.
Electrical behaviour of metals in salt solutions, 393.
—— conductivities, study of the chemical constitution of neutralisation of acids and bases by means of their, 2.
—— conductivity of a solution, alteration of, by addition of a non-electrolyte, 1382.
—— —— of lead dioxide, 672.
—— —— of organic acids, TRANS., 696.
—— —— of solutions of organic acids, influence of boric acid on, 256, 1265.
—— —— of substances in mixed solvents, 1038.
—— resistances, new method of measuring, 105.
—— volatility of the metals, 1037.
Electrocapillary phenomena, 553, 760.
—— reactions, 393, 394.
Electrochemical equivalent of copper, 105.
Electrodes, small, galvanic polarisation at, 759.
Electrolysis, 257.
—— and diffusion, theory of, 935.
—— laws of, 1037.
—— of potassium acetate solutions, TRANS., 10.
Electrolytes, changes of E.M.F. volume and temperature on mixing, 930.
—— correction in the calculation of the heat of dissociation of, 931.
—— separation of precipitates at the boundary of, 1038.
—— thermoelectric phenomena at the contact of two, 1037.
Electrolytic conductivity and dielectric power, coexistence of, 759.
—— —— of polybasic acids, 1145.
—— dissociation and absorbent power of coloured salts, 757.
—— —— and osmotic pressure, theories of, 1143.
—— —— of salts, determination of, by

means of solubility experiments, 1143.
Electrolytic gas, ignition temperature of, 680.
—— preparation of metallic alloys, 394.
—— separation of metals, new principle of, 1521.
Electromotive activity of the ions, 671.
—— force of gas batteries, 393.
—— —— relation of latent heat, specific gravity, &c., to, 257.
—— —— volume, and temperature, changes of, on mixing electrolytes, 930.
—— forces, new method of measuring, 105.
—— —— of metallic salts, 255.
Electrostenolysis, 393.
Element, new, in an Egyptian mineral, Trans., 491.
Elements, place of fluorine in the classification of, 11.
—— tabular expression of the periodic relation of, 562.
Endocarditis, infective, chemical pathology of, 744.
Energetics, studies on, 1149.
Energy as the unit of an absolute system of measurement, 1149.
Enzyme, cellulose-dissolving, search for, in the digestive tract of certain animals, Trans., 352.
Ephedra monostachia, ephedrine from, 893.
Ephedrine from *Ephedra monostachia*, 893.
Epichloramine, 29.
Epidibromhydrin, 420.
Equilibrium, chemical, in solutions, 1146.
—— labile conditions of, in mixtures of two substances at a temperature below the melting point of either, 936.
—— of chemical systems under unequal pressures, 937, 1148.
—— of double salts of lead and potassium iodides with their aqueous solutions, 560.
Erucic acid and brassidic acid, stereometric relations of, 429, 812, 1427.
—— —— bromo- and chloro-, 429.
—— —— dichloride, 429.
—— phenylhydrazide, 1428.
Errum hirsutum and *E. Lens*, composition of, 522.
Erythræa centaurium, constituents of, 1261.
Erythritol, thermochemistry of, 764.
Erythrocentaurin, 1262.
Essence of sandal wood, adulteration of, 1379.
Essences, detection of turpentine and other impurities in, 386.
Ethane, absorption-coefficient of, in water, 1044.
—— action of heat on, Trans., 329.
Ethanetetracarboxylic acid, symmetrical, 824.
Ethenyldiamidonaphthyl ethyl ether, 1098.
Ethenyldiamidotoluene and its derivatives, 837.
Ethenyldinitrotolnyleneamidine, 1197.
Ethenylnitrotoluyleneamidine, 1197.
Ethenylorthohomoparahydroxybenzenylazoxime, 321.
Ethenylparahomosalicenylazoximes, 319.
Ethenylpiperonylazoxime, 318.
Ethenyl-β-trichloro-α-hydroxypropenylazoxime, 321.
Ether, influence of, on the velocity of the hydrolytic action of yeast, Trans., 935.
—— solutions, dilute, cryoscopy of, 1045.
Ethereal oils, oxygen compounds of, 868.
Ethereal oils. See Oils.
Ethereal salts, action of sodium on, Proc., **1891**, 167.
—— —— condensation of cyanides with, 431.
—— —— in spirits, estimation of, 387.
Ethoxalylacetylfurfuramidine, 1007.
Ethoxalylacetyltolenylamidine, 1008.
Ethoxyacetamidoquinoline [1 : 4], 1104.
Ethoxyacetophenone, ortho-, 989.
Ethoxyamidoquinoline [1 : 4], 1105.
Ethoxyantipyrine, para-, 1080.
—— salicylate, 1082.
Ethoxyazobenzene, para-, preparation and nature of, 839.
—— reduction of, 839.
Ethoxybenzaldoxime, ortho-, 58.
Ethoxybenzonitrile, ortho-, 58.
Ethoxybenzylamine, ortho-, 58.
Ethoxy-α-bromocinnamene, ortho-, 989.
Ethoxybutyric acid, γ-, 813.
Ethoxycinnoline, 1494.
Ethoxycresol, 447.
Ethoxydiacetylorthophenylenediamine, meta-, 161.
Ethoxydihydroxyquinoxaline, meta-, 160.
—— para-, 734.
Ethoxydiphenylquinoxaline, para-, 732.
Ethoxydiphenylsulphoneorthophenylenediamine, meta-, 161.
Ethoxyhydroxydinitrodiphenylamine, 314.
Ethoxyhydroxymethylquinoxaline, 733.
Ethoxyimidofurfuran, 831.
Ethoxyisosuccinic acid, 1305.
Ethoxymetaxylenesulphonic acid, Proc., **1891**, 190.

Ethoxymethylindole, 955.
Ethoxynaphthazine, 733.
Ethoxyorthophenylenediamine, meta-, 160.
Ethoxyphenanthrazine, para-, 733.
Ethoxyphenyl sulphide, 1316.
Ethoxyphenylacetylene, 989.
Ethoxyphenylchloracrylic acid, ortho-, 989.
Ethoxyphenylhydrazine, para-, and its salts, 1080, 1081.
Ethoxyphenylhydrazinesulphonic acid, para-, 1082.
—— —— —— salts of, 1081.
Ethoxyphenylmethylpyrazolone, para-, 1080.
Ethoxyphenylnaphthostilbazonium chloride, action of ammonia on, 1247.
—— —— action of heat on, 1247.
—— hydroxide, 863.
Ethoxyphenylorthodiamidonaphthalene, 863.
Ethoxyphenylpropiolic acid, ortho-, 989.
Ethoxyphenylsulphonic acids, meta-, ortho-, and para-, and their derivatives, 1089.
Ethoxypiazthiole, para-, 734.
Ethoxypropanilide, α-, 1337.
Ethoxypyridine, α-, 109.
Ethoxyquinoline, derivatives of, 1105.
Ethoxyquinoxaline, para-, 732.
Ethoxyquinoxalinedicarboxylic acid, para-, 733.
Ethoxytetramethylenecarboxylic acid, Trans., 46.
Ethoxytrimethylammonium platinochloride, chlor-, 807.
Ethyl acetates, substituted, hydrolysis of, 1148.
—— acetoacetate, 140, 953.
—— —— acetyl and benzoyl, derivatives of, 817.
—— —— action of, on dicyanophenylhydrazine, 597.
—— —— action of phenylhydrazine on, 142, 953.
—— —— action of propylene bromide on the sodium derivative of, Trans., 67.
—— —— aldehydeuramides, 56.
—— —— constitution of, 583, 816, 1072.
—— —— haloïd, derivatives of, 697.
—— —— introduction of acid radicles into, 696.
—— —— magnetic rotation of, Trans., 808, 838.
—— —— stereoisomeric dioximes from, 1175.
—— β-acetoisobutyrate, 74.
Ethyl β-acetoxy-αβ-dibromopropionate, 817.
—— acetonedicarboxylate, 431.
—— —— magnetic rotation of, Trans., 812, 839.
—— acetoneoxalate, refractive and dispersive powers of, Trans., 854.
—— —— magnetic rotation of, Trans., 820, 853.
—— acetophenoneoxalate, magnetic rotation of, Trans., 833, 864.
—— acetosuccinate action of nitrous acid on, 1074.
—— acetothienoneoxalate, 154.
—— —— derivatives of, 303.
—— β-acetoxymethylacrylate, 817.
—— acetylcarbintricarboxylate, 145, 1070.
—— α-acetyl-β′-hydroxyhydromuconate, 143.
—— acetylmethyltrimethylenecarboxylate [1 : 2 : 1], Trans., 67.
—— acetyltartronate, 39.
—— alcohol, heats of combustion and formation of, 1139.
—— —— vapour tension of, 397.
—— allomethyl camphorate, ortho-, 1101.
—— allylacetoacetate, magnetic rotation of, Trans., 809.
—— amidoethylenedicarboxylate, Trans., 792.
—— β-amidocrotonate, magnetic rotation of, Trans., 828, 859.
—— —— refractive and dispersive powers of, Trans., 861.
—— amidomethylthiazolecarboxylate, 697.
—— 2 : 5-amidonitrobenzoate, 326.
—— amidothiazylisobutyrate, 697.
—— amidotolyloxamate, 1208.
—— anilacetoacetate, action of hydrocyanic acid on, 1196.
—— β-anilidoacrylate, 818.
—— 2 : 5-anilidonitrobenzoate, 326.
—— anilidophenylsuccinamate, 820.
—— anilidotrinitrophenylmalonate, 1218.
—— —— nitrite, 1217.
—— anilidotrinitrophenyltartronate, 1218.
—— azimethylenedicarboxylate, 453.
—— benzeneazocamphocarboxylate, 1344.
—— benzenesulphonate, 1220.
—— benzenesulphoneorthamidobenzoate, 334.
—— benzoparadifurfuran-α-dimethyl-β-dicarboxylate, 610.
—— benzoylacetate, action of propylene bromide on the sodium compound of Trans., 82.

Ethyl benzoylacetate, magnetic rotation of, Trans., 831, 861.
—— —— stereoisomeric dioximes from, 1175.
—— benzoylmethyltrimethylenecarboxylate, Trans., 84.
—— α-benzylacetoglutarate, 962.
—— benzyldicarboxyglutaconate, action of phenylhydrazine on, Trans., 795.
—— bromacetoacetate, 143, 818.
—— α-bromethylacetoacetate, 144.
—— bromide, bromination of, 577, 1414.
—— bromobenzenesulphonate (para), 1220.
—— α-bromocinnamates, action of phenylhydrazine on, Trans., 279.
—— bromodinitrophenylmalonate nitrite, 1219.
—— bromomalonate, action of potassium acetate on, 39.
—— α-bromomethylacetoacetate, 144.
—— bromopropyl ether, 420.
—— bromosuccinate, action of α- and β-naphthylamines on, 860.
—— bromotrinitrophenylmalonate, action of nitric acid on, 1217.
—— —— —— nitrite, 1217.
—— bromotrinitrophenyltartronate, 1218.
—— butyl ether, 28.
—— camphocarboxylate, 348.
—— —— action of sodium benzyloxide on, 74.
—— camphorate, 501.
—— camphorates and isocamphorates, 500.
—— carbacetoacetate, so-called, 819.
—— carbethoxyethylacetoacetate, 1179.
—— carboxyethylacetoacetate, 1070.
—— α-carboxyethylpimelate, 427.
—— chloracetate, action of sodium on, 953.
—— chloracetoacetate, constitution of, 697.
—— chlorobenzenesulphonate (para-), 1220.
—— chlorobromomalonate, 39.
—— chlorocarbonate, 963.
—— cinnamate, refractive power of, at different temperatures, Trans., 304.
—— citraconate, action of ethyl sodiomalonate on, 590.
—— cyanacetate, action of hydroxylamine on, 139.
—— —— action of, on aniline, 1072.
—— —— action of, on organic bases, 1071.
—— —— and benzaldehyde, condensation of, 1086.
—— γ-cyanacetoacetate, 819.
Ethyl cyanide, action of sodium on, 576.
—— α-cyanisopropyl ketoxime, 80.
—— cyanocinnamamate, 1087.
—— α-cyanocinnamate, 1086.
—— α-cyanopropionate, additive compound of hydrogen cyanide with, 1301.
—— cyanopyruvate oxime, 431.
—— cyanotricarballylate, 1181.
—— dehydrocholate, 741.
—— diacetoacetate, magnetic rotation of, Trans., 823, 854.
—— —— refractive and dispersive powers of, Trans., 857.
—— diacetosuccinate, action of nitrous acid on, 1074.
—— diallylacetonedicarboxylate, 434.
—— dibenzoylacetoacetate, 145.
—— dibenzylacetoacetate, 963.
—— dibenzylcarbamate, 1084.
—— dibromosuccinate, action of zinc on, 40.
—— dicarboxyglutaconate, action of ammonia on, Trans., 791.
—— —— action of phenylhydrazine on, Trans., 793.
—— dichloroketohydroxyhydrindenecarboxylate, 858.
—— dichloromalonate, 39.
—— dichloroquinoldiacetoacetate (para-), 609.
—— dichloroquinonediacetoacetate (para-), 609.
—— —— —— additive products of, 610.
—— diethoxyacetoacetate, 955.
—— dihydroxytartrate, 1181.
—— αβ-diisonitrosobutyrate, 1175.
—— dimethyldicyanoadipate, 430.
—— dimethyldicyanopimelate, 430.
—— dimethylsuccinosuccinate, 1182.
—— αβ-dimethylumbelliferonecarboxylate, 432.
—— dinitrophenylacetate, derivatives of, 178.
—— dioxosuccinate, 1181.
—— diphenoxymalonate, 40.
—— ditannacetoacetate, 181.
—— ditolylcarbamate (para-), 1084.
—— ethoxyacetoacetate, 954.
—— ethoxychloracetoacetate, 953.
—— ethoxyhydroxyquinoxalineacetate, 733.
—— ethoxyoxalacetate phenylhydrazone, 458.
—— ethylacetoacetate, magnetic rotation of, Trans., 809, 837.
—— α-ethylacetoglutarate, 962.
—— ethylideneacetoacetate, magnetic rotation of, Trans., 810, 837.

Ethyl ethylimidoethylphenylthiocarbamate, 466.
—— ethylurethanophenylacetate, 469.
—— formylacetate, acetyl and benzoyl derivatives of, 817.
—— —— constitution of, 816.
—— fulminurate, 690.
—— —— isomeric, 1417.
—— fumarate, action of ethyl sodiomalonate on, 590.
—— β-furfuramidocrotonate, 57.
—— hexyl ketone, 35.
—— hippurate, compound obtained by the action of sodium ethoxide on, 1002.
—— hydrazopropionate, 452.
—— hydrogen adipate, dissociation constant of, TRANS., 712.
—— —— camphorate, allo-, 1102.
—— —— dimethylmalonate, dissociation constant of, TRANS., 712.
—— —— ethylmalonate, dissociation constant of, TRANS., 712.
—— —— fumarate, dissociation constant of, TRANS., 714.
—— —— isosuccinate, dissociation constant of, TRANS., 712.
—— —— maleate, dissociation constant of, TRANS., 714.
—— —— malonate, dissociation constant of, TRANS., 711.
—— —— phthalate, dissociation constant of, TRANS., 714.
—— —— sebate, dissociation constant of, TRANS., 713.
—— —— suberate, dissociation constant of, TRANS., 713.
—— —— succinate, dissociation constant of, TRANS., 711.
—— β-hydroxyacrylate, 816.
—— —— hydroxybenzofurfuran-α-methyl-β-carboxylate (para-), 611.
—— β-hydroxycrotonate, acetyl and benzoyl derivatives of, 817.
—— hydroxytoluquinoxalineacetate, 709.
—— imidoethylphenylthiocarbamate, 466.
—— imidophenylthiocarbamate, 466.
—— imidosuccinamate, 820.
—— iodide, preparation of, TRANS., 717.
—— isobutyl ketone, 36.
—— —— —— oxidation of, 36.
—— isocamphorate, 501.
—— isopropyl ketone, 36.
—— itachloropyrotartrate, action of ethyl sodiomalonate on, 591.
—— itaconate, action of ethyl sodiomalonate on, 591.
—— ketacetate, 955.
—— licaryl ether, 1236.
Ethyl malate, inactive, 1431.
—— maleate, action of ethyl sodiomalonate on, 590.
—— malonate nitrosophenylhydrazide, 1004.
—— —— phenylhydrazide, 1004.
—— mandelate, 1089.
—— mesaconate, action of ethyl sodiomalonate on, 591.
—— mesoxalate, 40.
—— methoxybenzoylacetate (ortho-), 844.
—— methyl ketone, chloro-, action of sodium on, 810.
—— —— —— —— reactions of, 810.
—— β-methylacetosuccinate, action of nitrous acid on, 1074.
—— methylamphiglyoximecarboxylate, 1176.
—— methylcamphocarboxylate, 201.
—— 1 : 2-methylcarboxyethylpyrroline-acetate, 144.
—— methyl-α-cyanotricarballylate, 1182.
—— methyldiacetyladipate, TRANS., 73.
—— —— decomposition of, by heat, TRANS., 75.
—— methylsynglyoximecarboxylate, 1175.
—— morphine carbonate, 638.
—— β-naphthalenesulphonate, 1220.
—— β-naphthyl-β-amidoisobutyrate, 1342.
—— α-naphthylamidosuccinate, 860.
—— β-naphthylamidosuccinate, 860.
—— α-naphthylazoacetoacetate, 367.
—— α-naphthylidoacetate, 1341.
—— β-naphthylidoacetate, 1342.
—— α-naphthylidobutyrate, 1338.
—— β-naphthylidobutyrate, 1338.
—— α-naphthylidopropionate, 1337.
—— β-naphthylidopropionate, 1337.
—— nicotenylamidoximecarbonate, 208.
—— nitrate, action of alkaline solutions on, 692.
—— nitrosomethylisostrychnate, 1013.
—— oxalacetate, compound of, with phenylhydrazine, 49.
—— —— reduction of, 147.
—— oxalate, action of phosphoric chloride on, 588.
—— —— diphenylhydrazide, 981.
—— —— α-naphthylhydrazide, 511.
—— —— β-naphthylhydrazide, 509.
—— —— paratolylhydrazide, 512.
—— oximidoacetate, 700.
—— pentaneoctocarboxylate, 1316.
—— phenylacetate, amido-, 214.
—— phenylamidoacetate, 468.
—— —— nitrite, 469.
—— phenyl-β-azocrotonate, 143.

Ethyl phenylbiazolonecarboxylate, 513.
—— phenylcarbamate, nitration of, 712.
—— phenylhippurate, 468.
—— phenylhydrazidopropionate, 1456.
—— phenylhydrazilethylenedicarboxylate, Trans., 794.
—— phenylhydrazine-β-carboxylate, 145.
—— phenyl-β-hydrazocrotonate, 142.
—— phenylhydrazoneketophenylpyrazolonecarboxylate, 458.
—— phenylmethylpyrazolonecarboxylate, 798.
—— phenyl-β-naphthylcarbamate, 166.
—— phenylpyrazolonecarboxylate, Trans., 794, 798.
—— phenyltartronate, 40.
—— phenylthiouranilidacetate, 468.
—— phenyluramidoacetate, 468.
—— phenyluranilidacetate, 468.
—— piperazyloxamate, 211.
—— propanetetracarboxylate, 41.
—— propyl ether, 28.
—— —— ketone, oxidation of, 35.
—— quinoneoximecarboxylate, 1457.
—— santonate, amine of, 1353.
—— —— hydrazide of, 1353.
—— —— oxime of, 1352.
—— sodacetoacetate, 1428.
—— —— action of ethereal salts of unsaturated acids on, 590.
—— —— action of ethyl chlorocarbonate on, 1070, 1178.
—— —— constitution of, 140, 1178.
—— sodethylmalonate, action of acetic chloride on, 1179.
—— sodiocyanacetate, action of ethyl salts of unsaturated acids on, 1181.
—— sodiocyanotricarballylate, 1181.
—— sodiomalonate, action of ethereal salts of unsaturated acids on, 590.
—— sodium acetothiosulphate, 1419.
—— succinate phenylhydrazine, 1495.
—— succinic chloride, 1495.
—— tannacetoacetate, 181.
—— tetrachloro-α-hydroxyhydrindenecarboxylate, 858.
—— tetrahydroxysuccinate, 1181.
—— toluenesulphonate (para-), 1220.
—— toluidoacetate (ortho-), 1334.
—— —— (para-), 1335.
—— toluidoacrylate (β-para-), 818.
—— toluidobutyrate (α-ortho-), 1338.
—— —— (α-para-), 1338.
—— —— (β-para-), 818.
—— toluidopropionate (α-ortho-), 1337.
—— —— (α-para-), 1337.
—— tolylbiazolonecarboxylate (para-), 513.
—— triacetylacetate, 145.
—— trichloroparahydroxybenzofurfuran-α-methyl-β-carboxylate, 609.
Ethyl trichloroquinolacetoacetate, 608.
—— trichloroquinoneacetoacetate, 608.
—— trinitrophenylenedimalonate nitrite, 1219.
—— trithioacetate, 154.
Ethyl-γ-acetobutyric acid, γ-, 962.
Ethylacetovanillone, 61.
Ethylacetovanillonoxime, 61.
Ethylacetylacetone, magnetic rotation of, Trans., 813, 851.
Ethylacetylene, α-hydrobromide, 127.
Ethylacridine, 342.
Ethylaldoxime, action of azotoluene on, 1079.
—— action of diazobenzene on, 1079.
Ethylamidometanitrobenzophenone, para-, 336.
Ethylamidophenylnaphthylamine, action of benzaldehyde on, 1472.
Ethylamine hydrogen diaminechromium thiocyanate, 1000.
—— platinothiocyanate, 286.
—— thio-, salts of, 130.
—— thio-derivatives of, 130.
Ethylanilbiguanidine, 357.
Ethylaniline, action of silicon tetrachloride on, Trans., 455.
Ethylantibenzhydroximic acid, 463, 464.
Ethylbenzanilide, para-, 488.
Ethylbenzene, action of aluminium chloride on, 1309.
Ethylbenzenylamidine, 53.
Ethylbenzhydroximic acids, 462.
Ethylbenzophenone oxime, antipara-, 488.
—— —— synpara-, 488.
Ethylbenzoylcarboxylic acid, orthodichloronitro-, 1229, 1232.
—— —— —— lactone of, 1230.
Ethylbergaptic acid, 72.
Ethyl-δ-caprolactone, γ-, 962.
Ethylchitenidine, 1250.
Ethylcinnamylamide, β-brom-, 215.
Ethylcoumarin, α-, derivatives of, 330.
Ethylcoumarinic dibromide, 989.
Ethylcrotonic acid, oxidation of, 958.
Ethylcysteïn, 1111.
Ethyldimethylamidobenzene (6:1:4:3), Trans., 420.
Ethyldithiobiuret, α-, 704.
Ethylene, absorption coefficient of, in water and in alcohol, 1044.
—— action of heat on, Trans., 329.
—— explosion of, with less than its own volume of oxygen, Trans., 873.
—— flame, experiments on, Trans., 210.
—— glycol, thermochemistry of, 764.
—— nitrate, action of alkaline solutions on, 692.

Ethylene paratoluenethiosulphonate, 990.
—— sodium thiosulphonate, 1418.
Ethylenebenzenyldiamine, 1248.
Ethylene-derivatives of diazoamido-compounds, Proc., **1892**, 119.
Ethylenediamine, action of dithio-oxamide on, 1247.
—— action of, on thiamides, 1247.
—— platinothiocyanate, 287.
Ethylenephenylhydrazone, thionyl-, 1324.
Ethyleuxanthones, 1355.
Ethylfurfurylcarbamide, 43.
Ethylfurfurylthiocarbamide, 43.
Ethylhydroberberine, derivatives of, 1499.
Ethyl-δ-hydroxycaproic acid, salts of, 962.
Ethylhydroxypyrimidinecarboxylic acid, 1008.
Ethylidene bromide, bromination of, 1414.
Ethylideneacetophenone, trichlor-, 695.
Ethylidenecinchonic acid, 1490.
Ethylidenecinchoxinic acid, 1490.
Ethylidenedicyanophenylhydrazine, 597.
Ethylidenediphenylhydrazone, 1196.
Ethylisobutylthiocarbamide, symmetrical, 702.
Ethylisoformanilide, 708.
Ethylisosuccinimide, 701.
Ethylmalonic acid, bromo-, 40.
Ethylmercaptophthalimide, action of various reagents on, 130.
Ethylmetanitrobenzamide, β-brom-, 213.
Ethylmetanitrobenzenylamidine, 52.
Ethylmetaxylene, symmetrical, and its derivatives, 969.
—— unsymmetrical, and its derivatives, 968.
Ethylmethylamine, 64.
Ethylmethylketoxime, action of hydrocyanic acid on, 1196.
Ethylmethylmaleïc acid, 814.
Ethylmethylquinoline, 1107.
Ethyl-β-naphthindolesulphonic acid, sodium salt of, 1458.
Ethyl-β-naphthoxindole, 1458.
Ethylorthotoluidine, paramido-, 1078.
Ethylparisopropyltoluene, ortho-, 985.
Ethylphenol, ortho-, 1318.
Ethylphenylacetamide, β-brom-, 214.
Ethylphenylhydrazine acetoacetate, action of hydrocyanic acid on, 1196.
Ethylpseudocumene and its derivatives, 990.
Ethylpyridine, β-, properties and derivatives of, 629.
Ethyl-α-pyridone, 209.
Ethylpyrroline, α-, 351.
Ethylpyrroline, β-, 352.
Ethylpyrrolines, constitution of, 350.
Ethylquinidine, 1250.
Ethylquinolone, bromo- and nitro-derivatives of, 879, 880.
Ethylresorcinol ethyl ether, nitroso-, 45.
Ethylsulphone, diamido-, 131.
Ethylsulphonediphthalamic acid, 131.
Ethylsynbenzhydroximic acid, 463, 464.
Ethylthiobiuret, α-, 703.
Ethylthiocoumarin, α-, 330.
Ethylthiophen, β-, 829.
Ethylthiophenhydroximic acid, 831.
Ethylthiourea, action of nitrous acid on, Trans., 525.
Ethyltricarballylic acids, α-, 42.
Ethyltrihydroxybenzene, dinitro-, 315.
Ethylytrimethylammonium dibromo-, salts of, 806.
—— —— tribromo-, salts of, 807.
—— —— β-iodo-, salts of, 808.
Ethyltrimethylbenzenesulphonic acids, 990.
Ethyltrimethylenedisulphonesulphide, 593.
Ethyltrimethylenetrisulphone, 591, 593.
Ethylurethanophenylacetic acid, 469.
Ethylvinylpyridine, 1358.
Ethylxylenes, amido-, 969.
Ethylxylenesulphonic acids, 969.
Eucalyptus oil, terpin hydrate from, 1235.
Eupatorin, 1103.
Eupatorium perfoliatum, active principle of, 1103.
Eurhodoles, 859.
Euxanthic acid, 1354.
—— —— action of hydroxylamine on, 1355.
Euxanthone, 1354.
—— constitution of, 504.
Evaporation and condensation, spheres of, 956, 1149.
—— latent heat of, relation of specific inductive capacity to, 258.
—— under reduced pressure, apparatus for, 1386.
Excretion, nitrogenous, influence of water and sodium chloride on, 904.
—— of nitrogen and uric acid from the human system, influence of hot baths on, 1503.
—— of nitrogen in kidney disease, 743, 1504.
—— of nitrogen in urine, 1503.
Expansion of water, 7, 106, 1382.
—— thermal, of liquid bismuth, 259.
Explosion of ammonium nitrate, 683.
Explosives, 1141.
Extract, nitrogen free, constituents of, 653.
Extraction apparatus, 910.

F.

Fat, estimation of, in yolk of eggs, 1134.
—— estimation of, in milk, 549, 550, 1134, 1532.
—— estimation of, in the products from milk, 391.
—— extraction of, from milk solids, 391.
—— horse, 1533.
Fat-decomposing ferments in plants, 1261.
Fat-oils, absorption and digestion of, by plants, 1118.
Fats and oils, revision of constants employed in the analysis of, 547.
—— estimation of unsaponifiable matters in, 1533.
—— foreign, detection of, in butter, 1532.
Fauserite from Hodrusbánya, 1054.
Fencholenamine, 1240.
Fencholenic acid and its derivatives, 1237.
—— —— reduction of, 1237.
Fenchone and camphor series, 1236.
Fenchonitrile and its derivatives, 1236.
Fenchylamine fenchylcarbamate, 1239.
—— salts, 1239.
Fenchylcarbamide, 1239.
Fenchylphenylthiocarbamide, 1239.
Ferment, aërobic nitrate-reducing, in straw, 1259.
—— fibrin, 1112.
—— saccharific, localisation of, 517.
Fermentation, 820.
—— alcoholic, influence of oxygen and concentration on, Trans., 369.
—— —— influence of the hydrolytic action of yeast on its power of, Trans., 940.
—— conditions affecting the action of fluorides on, 906.
—— of arabinose with the *Bacillus ethaceticus*, Trans., 737.
—— of blood, 900.
—— of farmyard manure, 1123.
—— of mannitol and dextrose with *Bacillus ethaceticus*, Trans., 432.
—— of mannitol and dulcitol, a pure, Trans., 254.
Ferments, digestive, in crustacean eggs, 362.
—— fat-decomposing, in plants, 1261.
—— in pineapple juice, 650.
—— unorganised, 899.
Fern extract, ethereal, poisonous constituent of, 380.
Ferric chloride, action of barium peroxide on, 408.
—— —— action of, on metallic sulphides, 18, 278.
Ferric hydroxide, colloïdal solutions of, Trans., 152, 162.
—— oxychlorides, crystallised, 119.
—— phosphate, dissociation of, in presence of water and of saline solutions, 1292.
—— sulphate, anhydrous, crystallised, 943.
Ferrous solutions, action of iron on, 276.
Ferrum reductum, estimation of metallic iron in, 1524.
Fibre, vegetable, detection of, in silk or woollen tissue, 667.
—— —— woody, the pentosans of, 1420.
Fibres, specific gravity of, 1036.
Fibrin, decomposition of, in the human body, 904.
—— solubility of, 897.
Fibrin-ferment, 1112.
Fibrin-peptone, 1500.
Ficus carica, the latex of, 653.
—— *rubiginosa* and *F. macrophylla*, resins of, Trans., 916.
Filicic acid, 380.
Filicin, 380.
Filtration, hot, apparatus for, 1150.
—— use of asbestos in, 751.
Fir-wood, dextrose from, 801.
—— so-called artificial pectic acid from, 827.
Flame, coal-gas, flat, temperature of various parts of, Trans., 326.
—— structure of, Trans., 331.
Flame-coloration, origin of, Proc., **1892**, 8.
Flames, coal-gas, carbon deposited from, Proc., **1892**, 46.
—— —— —— luminosity of, Trans., 322.
—— luminous, structure of, Trans., 217.
—— non-luminous, experiments on, Trans., 205.
—— optical proof of the existence of suspended matter in, 111.
—— origin of acetylene in, Proc., **1892**, 47.
—— structure and chemistry of, Trans., 204.
—— the interactions occurring in, Proc., **1892**, 22.
Flashing points of heavy mineral oils, determination of, 542.
Flavin, preparation of, 503.
Fluoran, 970.
—— constitution of, 1228.
—— tribromo-, 970.
Fluoresceïn, constitution of, 1228.
Fluoresceïn-group, 1228.
Fluorescence, appearance of, in quinine salts, Trans., 789.

Fluorescin, 970, 1319.
—— ethyl ether, 1319.
Fluorides, action of boron on, 1153.
—— estimation of silicic acid in, 1127, 1128.
—— influence of, on fermentation, 906.
Fluorine, estimation of, 911.
—— in natural phosphates, 1055.
—— in recent and fossil bones, 1161.
—— place of, in the classification of the elements, 11.
—— proportion of, in fossil bones of various ages, 1413.
Fluoroform, 1316.
Fluoroline, 1492.
Fluorosulphonic acid, TRANS., 921.
Fluorovanadites, 785.
Fluoroxyhypovanadates, 785.
Fluoroxyvanadates, 785.
Fœtal organism, iron in the, 1502.
Fœtus, intake of the iron by the, 516.
Food, constituents, calorific value of, 4.
—— value of brushwood, 1511.
—— —— of the cotton plant, 1510.
Footeite, 415.
Formaldehyde, 423, 1423.
—— action of, on orthodiamines, 1496.
—— condensation products with, 1450.
—— nutrition of green plant cells with, 1259.
—— reactions of, 579.
—— thio-, reactions of, 579.
Formamidine picrate, 705.
Formanilide, action of trimethylene chlorobromide on, 1491.
—— metanitro-, 706.
Formates, metallic, 140.
—— trithiortho-, 611, 850.
Formic acid, heats of combustion and formation of, 1139.
—— —— thio-, 421.
Formoguanamine, formation of, 736.
Formohydroxamic acid, 699.
Formotoluidides, action of trimethylene chlorobromide on, 1491.
Formyl compounds, aromatic, derivatives of, 707.
Formyldiorthotolylhydrazine, 843.
Formyldiparatolylhydrazine, 843.
Formyldiphenylhydrazine, 843.
Formylorthotolylhydrazine, 843.
Fouqueite, 1056.
Frangulin, TRANS., 1.
—— composition of, TRANS., 3.
—— hydrolysis of, TRANS., 4.
—— preparation of, TRANS., 1.
Fraxetin, constitution of, 628.
Fraxin, constitution of, 628.
Freezing points, determination of, 765.
—— —— of cadmium, bismuth, and lead, lowering of the, when alloyed with other metals, TRANS., 888.
Freezing points of dilute solutions of cane sugar, 678, 1046.
—— —— of isomorphous mixtures, 396.
—— —— of very dilute solutions, determination of, 935.
Friedel-Crafts' synthesis, 337, 594.
Friedelite from Sweden, 1405.
Frog muscle, excitability of, in salt solutions, 515.
Fructose, d-, thermochemistry of, 763.
Fucose, thermochemistry of, 763.
Fulminuramide, 1417.
Fulminuric acid, 690, 1417.
Fumarates and maleates, action of *Penicillium glaucum* and *Aspergillus niger* on, 820.
Fumaric acid, complete transformation of, into maleïc acid, 1306.
—— —— transformation of maleïc acid into, 1305.
—— —— thermochemistry of, 1041.
Fungi, formation and physiological significance of oxalic acid in, 230.
Furfuraldehyde, condensation products of, with bases, 1451, 1452.
—— estimation of, 388.
—— estimation of, in spirits, 245.
—— formation of, from glycuronic acid derivatives and from albumin, 1433.
—— oximes of, 1433.
—— thio-, Cahours' polymeride of, 301.
—— α-trithio-, 301.
—— β-trithio-, 301.
Furfurallevulinic acid, δ-, 147.
Furfuramidine hydrochloride, 1006.
Furfuran compounds, 1006.
Furfuraniline, 1452.
Furfurantialdoxime, 1434.
Furfurimidoethyl ether, 1006.
Furfuronitrile, 831.
Furfuropinylamine, 997.
Furfursynaldoxime, 1433.
—— compound of, with phenyl cyanate, 1434.
Furfurylamine, 43.
—— nitro-, 43.
Furfurylcarbamide, 43.
Furfurylguanidine salts, 43.
Furfurylthiocarbamide, 43.
Furnace, combustion, new, 1514.
Furyl cyanide, 1006.
Furyldimethylhydroxypyrimidine, 1007.
Furylhydroxypyrimidinecarboxylic acid, 1007.
Furylmethylbenzylhydroxypyrimidine, 1007.
Furylmethylhydroxypyrimidine, 1006.
Furylphenylhydroxypyrimidine, 1007.
Fusel oil, estimation of, in spirits, 244, 543.

G.

Gadolinite, 1410.
Gadolinium earth, 1400.
Galactan, β-, 1171.
Galactonic acid, i-, 825.
—— —— l-, 826.
—— —— polarisation phenomena of, 1432.
Galactonolactone, polarisation phenomena of, 1432.
Galactose, i-, 826.
—— l-, 826.
—— thermochemistry of, 763.
Galena, analysis of, 662, 663, 1522.
—— estimation of sulphur in, 658.
—— separation of lead, silver, and zinc in, 1378.
Galipidine, 643.
Galipine, 642.
Galleïn, acetyl derivatives of, 1319.
Gallic acid, conversion of, into pyrogallol, 1314.
—— —— derivatives of, 715.
—— —— estimation of, in barks, 390.
—— —— estimation of, in urine, 924.
—— —— physiological action of, 904.
Gallium, spectrum of, 930.
Gallotannic acid, estimation of, in barks, 390.
Galvanic cell, practical form of the Latimer-Clark standard, 669.
—— —— standard, for small differences of potential, 670.
—— polarisation at small electrodes, 759.
Gambier, analysis of, 928.
Ganophyllite from Harstigen Mine, Sweden, 1412.
Garcinia mangostana, rind of, 205.
Garnierite from Norway, 1409.
Gas absorptions, improved pipette for, 1124, 1374.
—— analysis apparatus, clamps for, 524.
—— batteries, E.M.F. of, 393.
—— coal-, flame, experiments on, Trans., 205, 210.
—— —— flameless incandescence produced by, 768.
—— —— flames, carbon deposited from, Proc., **1892**, 46.
—— —— —— luminosity of, Trans., 322.
—— —— formation of ammonium sulphate by burning, 1389.
—— —— formation of sulphuric acid in burning, 1151, 1374, 1389.
—— —— heats of combustion of, 396.
—— compressed, pyrogenic hydrocarbons in, 797.
Gas pipette, improved, 1124, 1374.
—— water-, action of, on iron, Proc., **1891**, 126.
Gaseous mixtures, slow combustion of, 938.
Gases, absorption coefficients of, 1043.
—— absorption of, by liquids, 556.
—— determination of the specific gravity of, 1267.
—— diffusion of, lecture experiment on, 562.
—— dissolved in water, extraction of, 1526.
—— effusion of, lecture experiment on, 1150.
—— evolved in the fermentation of mannitol and dulcitol, Trans., 259.
—— heat of dissolution of, in liquids, 1042.
—— liquefied, determination of the density of, and of their saturated vapours, 934, 1043.
—— of peptone blood, 363.
—— solubility of, in water, 107, 271.
Gasometric investigations, levelling instrument for, 400.
Gasometry, use of potassium ferricyanide in, 526.
Gastric digestion, influence of amido-acids on, 742.
—— juice, estimation of hydrochloric acid in, 97.
Gas-volumeter, Proc., **1891**, 171.
Gas-volumetric analysis, 538.
Gelatin, decomposition of, in the human body, 904.
Genipa brasiliensis, crystalline constituent of, 1509.
Gentiana verna, substances contained in the petals of, 205.
Gentiol, 205.
Germination, action of boric acid on, 651.
—— of seeds, influence of vegetable poisons on, 228.
Gismondine from Westphalia, 1056.
Glanders, ptomaïne of, 1258.
Glass, action of superheated water and solutions of alkalis and of salts on, 1401.
—— action of water on, 120.
—— adhesion of mercury to, in presence of halogens, Trans., 452.
—— graphical chemistry of, 1158.
—— of slides and cover glasses, influence of the composition of, on the durability of microscopic objects, 1276.
—— solubility of, in cold water, 277.
—— suitable for chemical purposes, composition of, 410, 411, 1052.
—— wool, presence of lead in, 1375.

Glauber's salt, from the potash mines at Kalusz, 1286.
Glaucine, 893.
Glucoheptitol, α-, 1167.
Glucoheptonic acid, α-, 1166.
—— —— β-, 1168.
—— lactone, β-, 1168.
Glucoheptose, α-, 1166.
—— osazone, α-, 1167.
—— phenylhydrazone, α-, 1167.
Glucoheptose, β-, 1168.
—— phenylhydrazone, β-, 1168.
Gluconic acid, polarisation phenomena of, 1432.
Gluconolactone, polarisation phenomena of, 1432.
Gluconononic acid, 1170.
Gluconononitol, 1170.
Gluconononose, 1170.
Gluco-octitol, α-, 1170.
Gluco-octonic acid, α-, 1169.
—— ——β-. 1170.
Gluco-octose, α-, 1169.
—— phenylhydrazone, 1169.
Glucosamine, benzoyl derivatives of, 134.
Glucose, action of acetic anhydride on, 1293.
—— formation of, in the organism, 517.
Glucose, d-, thermochemistry of, 763.
Glucose. See also Dextrose.
Glucose-series, ascent of the, 1164.
Glutaconic acid, tetrachloro-, 1463.
Glutamic acid and its derivatives, 298.
Glutaric acid, action of hydroxylamine on derivatives of, 136.
—— —— decomposition of, at a high temperature, 40, 297.
—— —— pentachloro-, 1186.
—— —— thermochemistry of, 1041, 1141.
Glutarimide, 1484.
Glutarimidoxime, 138.
Glutimide, 298.
Glutin, peptone salts from, 895, 1016.
Glycerol, derivatives of, 288.
—— estimation of, by alkaline permanganate, 544.
—— estimation of, in sweet wines, 1263.
—— estimation of, in wine, 246, 1529.
—— fluorhydrins from, 799.
—— thermochemistry of, 764.
Glycerols, crude, analysis of, 544.
Glyceryl trinitrate, action of alkaline solutions on, 692.
Glycocine and its derivatives, 294.
Glycogen, estimation of, in the blood, 89.
—— formation of, in the liver from various sugars, 902.
Glycol, disodium derivative of, 421.
Glycol, thermal value of the hydroxyl groups in, 576.
Glycolaldehyde, preparation and properties of, 1424.
Glycoline, 633.
Glycollic acid, crystallography of, Proc., **1892**, 72.
—— —— preparation of, Proc., **1892**, 72.
—— anilide, Proc., **1892**, 72.
Glycolysis, hepatic, 89.
—— in blood, 900.
Glycuronic acid derivatives, formation of furfuraldehyde from, 1433.
Glyoxaline, 1493.
—— action of ethyl chloracetate on, 1493.
—— constitution of, 1326.
—— nitro-, 1493.
Glyoxalsulphonic acid, action of amido-bases on the sodium salt of, 1458.
Glyoxalylamidoformic acid phenylhydrazone, 442.
Glyoximecarboxylic acids, dissociation constants of, 1268.
Glyoximedicarboxylic acids, dissociation constants of, 1268.
Glyoximes, aliphatic stereoisomeric, 693.
Gmelinite from Nova Scotia, 21.
Gold, absorption of oxygen by, 943.
—— allotropic states of, 405.
—— and cadmium, compound of, Trans., 914.
—— electrolytic detection of, 541.
—— electrolytic separation of, from arsenic, from molybdenum, tungsten, and osmium, 920.
—— estimation of, by means of hydroxylamine hydrochloride, 662.
—— estimation of small quantities of, in base metals, 1525.
—— hydrosulphide, Trans., 135.
—— lowering of the freezing point of bismuth by, Trans., 897.
—— lowering of the freezing point of cadmium by, Trans., 902.
—— lowering of the freezing point of lead by, Trans., 909.
—— occlusion of hydrogen by, 567.
—— sulphide, natural, 283.
—— sulphides, organosols of, 775.
—— tin and cadmium, estimation of, in alloys, 1030.
—— use of cadmium in assaying, 919.
—— volumetric estimation of, 1526.
Gold. See also Auric.
Gold-bearing hot spring deposit, 24.
Gold-lead alloy, analysis of, Trans., 912.
Grape, chlorophyllic substances of the pericarp of the, 874.

Grapes, green, cause of the acidity of, 589.
Graphite, action of nitric acid on, 406,
—— artificial formation of, 407.
—— varieties of, 565.
Gravimetric analysis, simple and rapid method of, 524.
Gravivolumeter, Proc., **1891**, 171.
Grunerite from Michigan, 793.
Guanamine, synthesis of, 736.
Guanidine, amido-, and its derivatives, 1295.
—— nitrite, 53.
—— nitro-, 579, 951, 1295.
—— —— thermochemistry of, 1142.
—— occurrence of, in plants, 908.
—— picric acid as a reagent for, 950.
—— platinothiocyanate, 287.
—— salts, 1142.
—— test for, 926.
—— thermochemistry of, 1142.
Gulonic acids, i-, 822.
—— —— optically isomeric, 822.
Gulonolactones, 822.
Gulose, i-. 823.
Gum in plants which yields xylose on saccharification, 1371.
Gums which yield xylose, occurrence of, 380.
Guncotton, estimation of calcium and magnesium in, 1520.
Guvacine, 740.
—— nitroso-, 740.

H.

Hæmatin spectrum, sensitiveness of, 1369.
Hæmatite from the Hargita Mountains, 1054.
Hæmatoporphyrin, detection of, in urine, 1136.
—— in urine, 649.
Hæmatoporphyrinuria, 1118, 1506.
Hæmocyanin, 898, 1370.
—— respiratory value of, 1370.
Hæmoglobin, colloïdal solutions of, Trans., 157, 162.
—— colorimetric estimation of, 1264.
—— combination of, with oxygen, 1369.
Halogen salts, double, 779.
Haloïds, mutual displacement of the, 1270.
Haricot beans, cooked, composition of, Trans., 227.
Heat, expansion of water by, 1382.
—— latent, of evaporation, relation of specific inductive capacity to, 258.
—— —— of fusion of aluminium, 1281.
—— —— relation of E.M.F. to, 257.
—— mechanical theory of, recent developments of, 395.
Heat, of dissociation of electrolytes, correction in the calculation of, 931.
—— of dissolution and of osmotic pressure, theory of, 676, 765.
—— —— of gases in liquids, 1042.
—— —— of salts in water, 676.
—— of formation of hydrazine and hydrazoic acid, 261.
—— —— of permolybdic acid, 1383.
—— —— of platinic bromide and its principal derivatives, 3.
—— —— of potassium tricarballylates, 762.
—— —— of salts in alcoholic solution, 262.
—— of neutralisation of pyrogallol, 1446.
—— of vaporisation of a solution, 1382.
—— production in nerves during excitation, 365.
—— reconversion of, into chemical energy by production of water-generator gas and carbonic anhydride-generator gas, 673.
—— specific, of aluminium, 673, 1281.
—— —— of liquids, at temperatures above the boiling point, 761.
—— —— —— calculation of, 2.
—— —— of the diamond, 761.
Heat. See also Thermochemistry.
Heating power of coal, formulæ for calculating, 1143.
Heats of combination of bromine and iodine with magnesium, 762.
—— of combustion and formation of ethyl alcohol, formic acid, and acetic acid, 1139.
—— —— —— of nitrobenzenes, 4.
—— —— of cooked vegetables, Trans., 240.
—— —— of food constituents, 4.
—— —— of products of the distillation of coal, 395.
Heintzite from Leopoldshall, 791.
Helvine from Hungary, 1412.
Hemicelluloses, 907.
Hemipinic acid, meta-, 180.
Hemipinimide, bromo-, 1210.
Henbane seed, constituents of, 231.
Heptacetyl-α-glucoheptitol, 1168.
Heptane flame, experiments on, Trans., 210.
—— refractive power of, at different temperatures, Trans., 294.
Heptine, 1235.
—— action of sulphuric acid on, 967.
—— nature of, 1065.
—— nitrosochloride, 1235.
Heptyl acetate, secondary, 1162.
Hessite from Botes, 1054.
—— from Mexico, 793.

Heulandite- and desmine-groups, relations between minerals of the, 417.
Hexacetyl-α-glucoheptose, 1167.
Hexadecylacetylene, 1164.
Hexadecylene, bromo-, 1163.
Hexahydrobenzoic acid, properties of, 714.
Hexahydrodimethyldiazine, 507.
Hexahydronicotine, 1365.
Hexahydrophthalic acid, dibromotrans, 1216.
Hexahydrophthalic acid, synthesis of, TRANS., 172.
—— acids, thermochemistry of, 1041.
Hexahydropiperidinecarboxylic acid, 85.
Hexahydroxyaurin, 1470.
Hexamethyleneamine, action of ethyl chloracetate on, 1173.
—— action of sulphurous anhydride on, 1173.
—— benzochloride, 1173.
—— derivatives of, 1173.
Hexamethylenetetracarboxylic acid, dissociation constant of, TRANS., 706.
Hexamethyltriamidodiphenyltolylmethane, 190.
Hexamethyltriamidotriphenylarsine, 1321.
Hexane, nitration of, 575.
—— nitro-, 575.
Hexapropyltrimethylenetrisulphone, 592.
Hexenylsulphuric acid, 951.
Hexethyltrimethylenetrisulphone, 591.
Hexylacetylene, normal, 1064.
Homarus vulgaris, blood of, 648.
Homatropine, ψ-, 891.
Homoarecoline, 739.
Homocatechol, 1312.
—— and its nitro-derivatives, 1443.
Homocumic acid, paradibromo-, oxidation products of, 604.
Homogentisic acid, estimation of, in urine, 925.
Homolevulinic acid, 961.
Homologous compounds, vapour tension of, 396.
Homonapelline, TRANS., 393.
Homoparahydroxybenzaldehyde, ortho-, 320.
Homoparahydroxybenzaldoxime, ortho-, 320.
Homoparahydroxybenzenylamidoxime, ortho-, 320.
Homoparahydroxybenzonitrile, ortho-, 320.
Homoparahydroxybenzophenylhydrazone, ortho-, 320.
Homopiperonic acid, α-, 47.
Homosalicenylamidoxime, ortho-, 320.
—— para-, 319.
Homosalicylaldehyde, ortho-derivatives of, 320.
Homosalicylaldoxime, ortho-, 320.
—— para-, 318.
Homosalicylamide, para, 318.
Homosalicylic acid, para-, derivatives of, 318.
Homosalicylonitrile, ortho-, 320.
—— para, 319.
Homosalicylphenylhydrazone, ortho-, 320.
Homosalol, 1092.
Horse fat, 1533.
Hübnerite, 793.
Human *succus entericus*, 1368.
—— system, influence of hot baths on the excretion of nitrogen and uric acid from the, 1503.
—— urine, normal, reducing agents in, 1503.
Humic acid, properties of, 1373.
—— —— spontaneous oxidation of, 655.
Humin, properties of, 1373.
Hungarian minerals, 1054.
Hydantoïns and bases derived from them, 149.
—— γ-substituted, 827, 828.
Hydracetine, paralkyloxy-derivatives of, 1080.
Hydrastine, 223.
—— reactions of, 755.
Hydrazides, 843, 981.
—— acid, 710.
Hydrazine, heat of formation of, 261.
—— hydrate, molecular refraction of, 934.
—— nitride, 113.
—— thermochemistry of, 933. 1143.
Hydrazineamidoditolyldisulphonic acid, 1468.
Hydrazine-residue, displacement of, by halogens, 842.
Hydrazines, aromatic, action of the chlorides of phosphorus, arsenic, boron, and silicon on, 1324.
—— of quinoline, TRANS., 782.
—— secondary asymmetrical, 456.
Hydrazobenzenedisulphonamide, 973.
Hydrazobenzeneorthocarboxylic acid, 67.
—— —— parachlor- and parabrom-, 68.
Hydrazo-compounds, intramolecular change in, 840.
Hydrazodicarbonamide, 1298, 1429.
Hydrazodicarbonamidine nitrate, 1298.
Hydrazoic acid, heat of formation of, 261.
Hydrazomethylethylisoxazole, 79.
Hydrazones, action of hydrocyanic acid on, 1195.
—— aromatic, and thionyl chloride, 1324.

Hydrazones, isomeric, 1083.
Hydrazoorthodichlorodibenzyl alcohol, 444.
Hydrazophenetoïl, para-, 159.
Hydrazopropionylhydrazine, 452.
Hydrazotoluene, para-, formation of an orthamidotolylamine from, 853.
Hydrazotoluenedisulphonamide, 1468.
Hydrindone, formation of derivatives of, from halogen cinnamic acids, 1222.
—— orthobrom-, 1222.
—— parachlor-, 1222.
—— paraiodo-, 1222.
Hydriodic acid and hydrogen peroxide, catalytic influence of acids on the velocity of the reaction between, 110.
Hydriodoapoquinine, 82.
Hydriodoquinine, 82, 640.
Hydroantipyrine, 731.
Hydrobenzoic acids, 714, 847.
Hydroberberine, 1498.
—— ethiodide and related compounds, 1499.
Hydrobromic acid, preparation of, 270.
—— —— pure, preparation of, Trans., 97.
Hydrobromic acid. See also Hydrogen bromide.
Hydrocarbon derived from perseïtol, 1065.
Hydrocarbons and their halogen derivatives, saturated and unsaturated, method of determining the constitution of, 285.
—— aromatic, action of aluminium chloride on, 1309.
—— —— displacement of hydrogen by haloïds in, 1310.
—— closed-chain, action of sulphuric acid on, 967.
—— decomposition of, with steam, 288.
—— flames of, Trans., 204, 210, 212.
—— of the methane series, nitration of, 575.
—— pyrogenic, in compressed gas, 797.
—— unsaturated, and phenols, condensation of, 446, 1443.
—— vegetable, natural synthesis of, 1234.
Hydrochelidonamic acid, 432.
Hydrochelidonanilic acid, 433.
Hydrochelidon-bismethylimide, 433.
Hydrochelidonic acid, 432.
—— —— dioxime, 434.
Hydrochelidonimide, 433.
Hydrochloric acid, estimation of, in stomach contents, 326, 1125.
—— —— estimation of, in the gastric juice, 97.
—— —— free, in the stomach, estimation of, 236.
Hydrochloric acid tables, revised, 11.
Hydrochlorodimethylpyrone, 811.
Hydrochloro-α-methyltropidine, 358.
Hydrocinnamenylacrylic acid, 988.
—— —— oxidation of, 986.
Hydrocinnamic acid, parachlor-, 1222.
Hydrocotoïn, reactions of, 62.
Hydrocoton, nature of, 873.
Hydrocoumarone, 1318.
Hydrodiffusion, theory of, 935.
Hydrofluoranic acid, 1228.
Hydrogen, absorption coefficient of, in alcohol, 1043.
—— and oxygen, admixed, slow combustion of, 562, 938.
—— behaviour of, towards lead and other metals, 567.
—— bromide, action of sulphuric acid on, Trans., 99, 100.
—— cyanide, action of, on mercurous salts, 1416.
—— —— detection of, 361.
—— —— estimation of, 1530.
—— flame, experiments on, Trans., 215.
—— Hasselberg's so-called second or compound spectrum of, 1381.
—— maximum tension with which, is set free from solutions by metals, 561.
—— nitride, synthesis of, 1151.
—— occlusion of, by lead, 942.
—— —— by metals, 567.
—— —— by palladium, lecture experiment, 563.
—— peroxide, action of iodine and its oxy-acids on, 539.
—— —— action of, on magnesium, 17.
—— —— action of, on the hydrated oxides of cadmium, zinc, and magnesium, 1278.
—— —— and hydriodic acid, catalytic influence of acids on the velocity of the reaction between, 110.
—— —— and potassium permanganate solutions, reaction between, 277.
—— —— detection of, 1124.
—— —— estimation of, 526.
—— —— separation of metals in alkaline solution by, 537.
—— —— solutions, preparation of, 270.
—— —— test for, 381.
—— —— use of, in analysis, 1031.
—— phosphide, action of, on an ethereal solution of bismuth tribromide, 279.
—— reaction of, with chlorine and oxygen, 1147.
—— solubility of, in water, 108.
—— sulphide, absorption coefficient of, in water, 1044.

Hydrogen sulphide flame, experiments on, TRANS., 216.
—— structure of, 1381.
Hydrolopachol, chlor-, TRANS., 631.
—— dibromo-, TRANS., 643.
Hydrolytic action of yeast, velocity of, TRANS., 928.
Hydronaphthoic acids, 191.
Hydrophthalic acids, 1211.
Hydrosorbic acid, oxidation of, 959.
Hydrosulphides, metallic, TRANS., 114.
Hydrotannic acid, 181.
Hydroxamic acid derivatives, isomeric, 711.
—— acids, 461.
—— —— aliphatic, new method of preparing, 698.
—— —— constitution of, 300, 461.
—— —— of the fatty acids, 828.
Hydroximic acids, 462.
Hydroximidomethylsynoxazolone, 1175.
Hydroximidophenylsynoxazolone, 1177.
Hydroxy-γ-acetoisovaleric acid, β-, 325.
Hydroxyacetophenone and its derivatives, 845.
Hydroxyacetylpæonol, 846.
Hydroxy-acids and lactones, reciprocal transformations of, 1303.
—— —— α-, and orthodiamines, constitution of the compounds obtained from, 1359.
Hydroxyaldehydes, ortho-, action of acetic chloride on, 1458.
Hydroxyamidobenzophenone, 1227.
Hydroxyamidothymoquinone, 1093.
Hydroxyanthranol, 346.
Hydroxyaurin, 1469.
Hydroxyaurincarboxylic acids, 1469.
Hydroxyaurindicarboxylic acid, 1469.
Hydroxyaurins and their carboxylic acids, 855.
Hydroxyazo-dyes, ortho-, constitution of, 506.
Hydroxybenzaldiphenylmaleïde, 483.
Hydroxybenzenes, condensation of, with nitrobenzaldehydes, 621.
Hydroxybenzofurfuran-α-methyl-β-carboxylic acid, trichloropara-, 609.
Hydroxybenzoic acids, action of heat on, 1208.
Hydroxybenzophenone, 309.
—— meta-, and its oximes, 490.
—— para-, and its oximes, 489, 490.
Hydroxybenzylidenefenchylamine, 1239.
Hydroxybenzylideneorthamidophenol, 1451.
Hydroxybenzylideneparamidophenol, 1451.
Hydroxybenzylidenepinylamine, para-, 997.
Hydroxy-β$_1$-bromo-γ$_1$-methyljuloline, α$_1$-, 497.
Hydroxybutanedisulphonic acid, 424.
Hydroxybutane-β-sulphonic acid, sodium salt of, 424.
Hydroxybutyric acid, α-chloro-β-, 295.
—— —— β-chlor-α-, 296.
—— —— γ-trichloro-β-, 429.
—— —— γ-, transformation of, into its lactone, 1303.
Hydroxycaprolactone, 959.
Hydroxycarbon compounds, action of non-metallic nitrides and hydronitrides on, 1311.
Hydroxy-3-chloroquinoline, 4-, 877.
—— methohydroxide, 1-, 878.
Hydroxycinnoline, 1494.
Hydroxydimethylquinoline, 729.
Hydroxydinitrodiphenylamine, 310.
Hydroxydiphenylquinoxaline, para-, 733.
Hydroxyditolyldisulphonic acid, amido-, 1468.
Hydroxydixanthones, 504, 1097.
Hydroxyethyl sodium thiosulphate, 1418.
Hydroxyethylbenzoic acid, orthochloronitro-, lactone of, 1230.
Hydroxyglutaric acid, β-, 147.
Hydroxyhydrindenecarboxylamide, tetrachlor-α-, 858.
Hydroxyhydrobenzoïns, diortho-, isomeric, 167.
Hydroxyhydrocyanomesitenelactone, 325.
Hydroxyhydroisohydracetic acid, nitrile of, 325.
Hydroxyhydrolapachol, TRANS., 628.
Hydroxyisoquinolines and their derivatives, 877.
Hydroxyketone-dyes, 1224.
Hydroxyketones, aromatic, 62.
—— —— behaviour of, with sulphuric acid and with ammonia, 1226.
Hydroxylamine, alkyl derivatives of, 316, 1456.
—— constitution of, 1392.
—— crystallised, preparation of, 771, 1391.
—— preparation and properties of, 402, 1391.
—— thermochemistry of, 1143.
Hydroxylamine-derivatives, so-called physically isomeric, 711.
Hydroxy-β-lapachone, TRANS., 649.
Hydroxymetamethoxybenzoylcarboxylic acid, para-, 64.
Hydroxymetanitrobenzaldehyde, para-, 336.
Hydroxymethylbenzoic acid, ortho-, 715.
—— —— rate of transformation of, into phthalide, 1270.
Hydroxy-γ$_1$-methyl-β$_1$γ$_1$-dibromojuloline, α$_1$-, 497.

Hydroxymethyleneacetone, stereoisomerism of, 1073.
Hydroxy-γ_1-methyljuloline, α_1-, 497.
Hydroxymethylquinoline, metamido-ortho-, 506.
Hydroxymethylquinolines, 727, 728.
—— nitro-, 727, 728, 729.
Hydroxy-α-naphthaquinone, preparation of, 1098.
Hydroxynaphthoïl anilide, β-, 1476.
Hydroxy-β-naphtho-xanthone, 3′-, 1099.
Hydroxynaphtho-xanthones, 1100.
Hydroxynaphthyl trihydroxyphenyl ketone and its derivatives, 1226.
Hydroxynitrobenzyldiphenylmaleïde, 485.
Hydroxynitrobenzyldiphenylmaleïmidine, 486.
Hydroxynitroquinoline [1:4-], 1105.
Hydroxyoxindole chloride, amido-, 1219.
Hydroxyphenanthrazine, para-, 733.
Hydroxyphenanthridine, 197.
Hydroxyphenonaphtho-xanthone, 1099, 1100.
Hydroxyphenylhydrindone, 1221.
—— hydrazone, 1221.
Hydroxyphenylhydrocoumarin and its isomerides, 849.
Hydroxyphenylpyridone, $\beta\beta$-dichloro-α-, 449.
Hydroxyphenylpyridonecarboxylic acid, $\beta\beta$-dichloro-α-, 448.
Hydroxypiazthiole, para-, 734.
Hydroxypimelic acid, 423.
Hydroxypiperidine, α-, 1485.
Hydroxypropenylamidoxime, β-trichloro-α-, 321.
Hydroxypropylparadibromobenzoic acid, 604.
Hydroxy-β-phthalimidoethyl sulphide, β-, 130.
Hydroxypyridine, α-, 208.
Hydroxypyruvic acid, osazone of, 356.
Hydroxyquinoline, 4:1-brom-, 354.
—— 4:3:1-dibrom-, 354.
—— 1-, methohydroxide, 878.
—— 2-, methiodide, methochloride, and methohydroxide, 876.
—— 4:3-brom-, 353.
Hydroxyquinolines, halogen alkyl compounds of, 876.
Hydroxyquinones, 1098.
—— formation of, from quinones, 45.
Hydroxyquinoxaline, para-, 732.
Hydroxytetrahydrobenzyldimethylamine, Δ^3-, 359.
Hydroxytetrahydronaphthoic acid, bromo-, lactone of, 193.
Hydroxytetramethylenecarboxylic acid, Trans., 44.
Hydroxythymoquinone, 1098.
Hydroxy-$\beta_1\beta_1\gamma_1$-tribromo-γ_1-methyljulolidine, α_1-, 498.
Hydroxyvaleric acid, γ-, transformation of, into its lactone, 1303.
Hydroxyvalerolactone, 958.
Hydroxyxanthones, 504, 1096, 1100.
—— of the naphthalene and quinoline series, 1098.
Hyoscine, 1255, 1366, 1498.
—— composition of, 1498.
Hyoscyamine, existence of, in the lettuce, Trans., 90.
Hypophosphates, 403.
Hyposantonic acid, 870, 1353.
Hyposantonin, 870.
Hypoxanthine, 220.

I.

Imidazole, 313.
Imidazoles, 1326.
Imidazolone, μ-, 1327.
Imidazolyl mercaptan, μ-, 1328.
—— methyl sulphide, μ-, 1328.
Imides, substituted, modes of formation of, 1204.
Imidoacetates, constitution of, 982.
Imidodiazoles, 313.
Imidole, 312.
Imidosulphonamide, Trans., 952.
Imidosulphonates, Trans., 943.
Imidosulphonic acid, Trans., 945.
—— acids, 700.
Imidothiocarbamates, 465.
Inanition, bile during, 225.
Incandescence, flameless, produced by coal gas, 768.
Indazole-derivatives, 67.
Indigo-blue, products from, 991.
Indigodisulphonic acid, synthesis of, 69.
Indigo-green, 991.
Indium hydrosulphide, Trans., 134.
Indole, nitroso-, molecular weight of, 67.
—— synthesis of, from tartaric acid and aniline, 66.
Indoles, substituted, formation of, 1465.
Indothymol, 1311.
Indoxazen, 993.
Indoline-group, 341.
Indulines, 492.
—— formation of, 1476.
Inositol, thermochemistry of, 764.
Inulin, thermochemistry of, 764.
Invertebrates, blood of, 648.
Iodates, estimation of, in potassium iodide, 657.
Iodic acid and its salts, 1388.
—— —— use of, in quantitative analysis, 1027.
Iodides, estimation of, 527.

Iodine, action of, on potassium chlorate, Trans., 925.
—— action of, on potassium sulphite and thiosulphate, Trans., 1083.
—— action of, on sodium hydrogen sulphite, 681.
—— and its oxy-acids, action of, on hydrogen peroxide, 539.
—— bromine and chlorine, exchange of, between inorganic and organic haloïd compounds, 574.
—— —— —— separation of, 1028.
—— chlorine compounds of, 1387.
—— detection of bromine and chlorine in presence of, 1514.
—— fixation of, by starch, 578.
—— free, estimation of, 539.
—— heat of combination of, with magnesium, 762.
—— solubility of, in chloroform, 769.
—— trichloride, 1388.
Iodochromate, 124.
Iodoform, estimation of, 1528.
Iodometry, 1514.
Iolite, composition of, 793.
Ions, colour of the, 1137.
—— electromotive activity of the, 671.
Iridium, removal of platinum from, 1285.
Iron, action of carbonic oxide on, 568.
—— action of chlorine and of bromine on, 118.
—— action of nitric acid on, 1278.
—— action of nitric oxide, on, 1152.
—— action of water gas on, Proc., 1891, 126.
—— ammonium sulphates, 943.
—— and aluminium, estimation of, by the Glaser method, 755.
—— —— estimation of, in the presence of phosphoric acid, 755.
—— cast, calorimetric researches on the condition of silicon and aluminium in, 19.
—— calorimetric estimation of, 240, 1132.
—— direct estimation of aluminium in, 102.
—— distribution and condition of, in barley, 1509.
—— electrolytic separation of, 917.
—— estimation of carbon in, 913, 1030.
—— estimation of, in aluminium, 1131.
—— estimation of, in phosphates, 536.
—— estimation of manganese in, 916, 1030, 1514.
—— estimation of phosphorus in, 528, 529, 911.
—— estimation of sulphur in, 1376.
—— Hamburger's method for the estimation of small quantities of, 1525.
—— in bone-black, 1053.
Iron, intake of, by the fœtus, 516.
—— in the fœtal organism, 1502.
—— in the liver, 1503.
—— manganese, and calcium, separation of, 916.
—— metallic, estimation of, in *ferrum reductum*, 1524.
—— native, from Cañon Diablo, 947.
—— occlusion of hydrogen by, 567.
—— pig, estimation of phosphorus in, 912.
—— —— estimation of sulphur in, 382.
—— precipitation of copper by, 276.
—— salts, action of alkaline polysulphides on, 537.
—— —— utilisation of burnt pyrites in the preparation of, 1281.
—— separation of, from cobalt, nickel, and manganese, 103.
—— testing, for arsenic, 1030.
—— volumetric estimation of, 240.
—— wrought, estimation of slag in, Trans., 551.
Iron-ores, estimation of phosphorus in, 529,
—— —— genesis of, by replacement of limestone, 126.
—— —— of Central Russia, 689.
—— —— of the Marquette district, Michigan, 794.
Iron. See also Ferric and Ferrous.
Isaldoxime-derivatives, intramolecular change of, 50.
Isidiomatic compounds, 1366.
Isoamyl alcohol, vapour tension of, 397.
—— iodide, action of, on trimethylamine, 805.
Isoamylaniline, 44.
Isoamylbenzene, 985.
Isoamylene, condensation of, with phenols, 446.
Isoamylguanamine, formation of, 736.
Isoamylparisopropyltoluene, ortho-, 985.
Isoamylthymol, 446.
Isoanemonic acid, 1241.
Isoanemonin, 1241.
Isoanilides, 705.
Isoantipyrine, 635.
Isoapiole, derivatives of, 1315.
—— nitrosite, 447.
Isoapoquinine, 82.
Isoarabic acid, 1180, 1432.
Isobenzaldiphenylmaleïde, 486.
Isobenzaldiphenylmaleïmidine, 486.
Isobutaldehyde, action of zinc and ethyl chlorocetate on, 1300.
—— chlor-, 1292.
Isobutyl alcohol, action of bromine on, 809.

Isobutyl alcohol, action of chlorine on, 1292.
—— —— vapour tension of, 397.
—— iodide, action of, on trimethylamine, 805.
Isobutylallylamine, 31.
Isobutylallylphenylcarbamide, 31.
Isobutylallylphenylthiocarbamide, 31.
Isobutylamine, chloro- and dichloro-, 1172.
Isobutylbenzene (b. p. 165—170°), 44.
Isobutylbenzyl orthoxylyl ketone, 338.
Isobutylbenzylparatolylcarbamide, 1084.
Isobutyldibenzylcarbamide, 1083.
Isobutylisobutylideneamine, 1173.
Isobutylparaditolylcarbamide, 1083.
Isobutylparisopropyltoluene, ortho-, 985.
Isobutylphenylhydrazone, thionyl-, 1324.
Isobutylphenylthiocarbamide, symmetrical, 702.
Isobutylpropargylamine, 32.
Isobutylpropylamine, 32.
Isobutyric acid, bromo-, action of ammonia on, 1302.
—— diphenylhydrazide, 981.
—— phenylhydrazide, 981.
Isocamphenol, properties of, 199.
Isocamphor, 199.
Isocarbostyril, 882.
Isocarbostyrilcarboxylic acid, 882, 970.
Isocinchonidinesulphonic acid, 514.
Isocinchonine, 222.
Isocinchoninesulphonic acid, 515.
Isoconchininesulphonic acid, 514.
Isocoumarincarboxylic acid, 970.
Isocrotonaldehyde, presence of, in a brandy, 810.
Isocrotonic acid, derivatives of, 295.
—— —— oxidation of, 957.
Isocyanates, aromatic, 832.
Isocyanides, refractive powers of, 757.
Isocyanoparatolyl dichloride, 1442.
Isocyanophenyl dichloride, 1439.
Isocyanorthotolyl chloride, 1441.
Isodehydrocholal, 741.
—— chloro-, 741.
Iso-β-dichlorhydrin metahydroxybenzoate, 471.
Isodihydroxybutyric acid, 958.
Isodihydroxycaproic acid, salts of, 959.
Isodissociation, laws of, 3.
Isoerucic acid, 812.
Isoethenyldiamidotoluene, derivatives of, 838.
Isoeugenol and its derivatives, 45.
Isofenchonoxime, β-, 1237.
Isohexeric acid, 958.
Isohydrotannic acid, 182.
Isohydroxycaprolactone, 959.
Isohyposantonic acid, 870.
Isohyposantonin, 870.
Isomalic acid, 824.
Isomaltose, 1293.
Isomangostin, 206.
Isomerism, special case of, 1067.
Isomethylpæonol, 846.
Isomorphous mixtures, freezing point of, 396.
Isonaphthazarin, 494, 720.
Isonipecotinic acid, 1486.
Isonitroso-compounds, action of sulphurous acid on, 475.
Isoparaxylalphthalide, 474.
Isoparaxylalphthalimidine, 474.
Isophthalamidine nitrite, 53.
Isophthalic acid, asymmetrical amido-1464.
—— —— —— bromo-, 337.
—— —— parachloro-, 1201.
Isoprene, spontaneous conversion of, into caoutchouc, 1482.
Isopropane, nitro-, action of methyl iodide and chloroform on, 1290.
Isopropyl alcohol, action of bromine on, 809.
—— —— and sodium, thermochemistry of, 674.
—— —— properties of, 691.
—— sodium thiosulphate, 1418.
Isopropylacetothienone, β-, 442.
Isopropylbenzene, action of aluminium chloride on, 1309.
Isopropylbenzophenone and its oximes, 489.
Isopropylcoumarin, α-, derivatives of, 330.
Isopropyleneparamidophenol, 1451.
Isopropylmalic acid, 428.
Isopropylphthalimide, 158.
Isopropylpropiothienone, β-, 443.
Isopropylthiocoumarin, 330.
Isopropylthiophen, β-, 442.
—— mercuric chloride, β-, 829.
Isopropyltricarballylic acid, 42.
Isoquinine, 82.
Isoquininesulphonic acid, 514.
Isoquinoline methiodide, oxidation of, 730.
—— preparation of, from naphthalene, 882.
—— pyrogenic synthesis of, 739.
—— sulphonation of, 876.
Isosaccharin, specific rotatory power of, 1421.
Isosafrole, action of nitrous acid on, 1198.
—— action of potash and methyl alcohol on, 972.
—— nitrosite, 447.
—— oxidation of, 310, 328.
—— the oxymethylene group in, 972.
Isosafroledioxime peroxide, 1198.
Isosantinic acid, 872.

Isostrychnic acid, isonitroso-, 1012.
Isosuccinic acid, bromo-, action of alcoholic potash on, 1305.
—— —— thermochemistry of, 1140.
Isosuccinimide, alkyl derivatives of, 701.
Isoterpene from the resin of *Pinus abies*, 625.
Isothermal curves for carbonic anhydride, 3.
Isothermals, change of the empirical and theoretical, of mixtures of two substances with the temperature, 259.
Isovaleric acid, α-bromo-, 427.
Isovaleridenetoluidine, 1194.
Isoxazoles, 506.

J.

Jacobsite from Sweden, 1404.
Julole, 496, 883.
Julole-violet, 498.
Julole-violet-base, 499.
Julolidine, 1492.

K.

Kamacite from the Welland meteoric iron, 24
Kamés, relation between truffles and, 654.
Kaolin, estimation of, in arable soils, 1026.
—— from Colorado, 1406.
—— in arable soil, 1026.
Karlsbad salts, analysis of, 659.
Keto-γ_1-benzoxyjuloline, α_1-, 884.
Keto-γ_1-chlorojuloline, α_1-, 884.
Ketodimethyldihydroquinoxaline, 1108.
Keto-β_1-ethyl-γ_1-methyljuloline, α_1-, and its bromo- and nitro-derivatives, 883.
Ketohydroxyhydrindenecarboxylamide, dichloro-, 859.
Keto-γ_1-hydroxyjuloline, α_1-, 884.
Ketomethylbenzyldihydroquinoxaline, 1108.
Ketomethylethyldihydroquinoxaline, 1108.
Keto-γ_1-methyljulolidine, α_1-, 497.
Ketomethyljuloline, dyes obtained from, 498.
—— oxidation and reduction of, 496.
Ketomethylphenyldihydrophenoquinoxaline, 1108.
Ketones, action of paramidodimethylaniline on, 854.
—— action of potassium cyanide on halogen derivatives of, 324.
—— action of sodium on, 169.
—— aromatic alkyl, and their oximes, 985.
Ketones, aromatic, metallic compounds of, 1205.
—— —— nitro-, preparation of, 1459.
—— bromo-, formation of, by the action of bromine on the alcohols of the ethyl series, 809.
—— colour reaction of, with aromatic nitro-compounds, 1263.
—— compounds of, with mercuric chloride, 828.
—— condensation of chloral with, 694.
—— fatty, action of chlorine on, 424, 810.
—— —— mixed, oxidation of, 35.
—— of the quinoline series, 1488.
—— physiological action of, 1506.
—— sodium nitroprusside as a reagent for, 924.
—— unsaturated γ-, action of phenylhydrazine on, 995.
Ketonic acids, oximes of, 327.
Ketonic compounds, magnetic rotation of, TRANS., 800.
Ketonic oxygen, estimation of, 546, 1530.
—— —— substitution of the azo-group for, 451.
Keto-β_1-nitroso-γ_1-hydroxyjuloline, α_1-, 884.
Ketophenyl-γ-piperidone, pentachloro-α-, 449.
Ketoquinazolines, new synthesis of, 1495.
Ketoximes, aromatic alkyl, 1200.
—— —— influence of substituting radicles on the configuration of, 487.
—— configuration of, 426.
Ketoximic acids, γ-, configuration of, 1202.
Kidney disease, excretion of nitrogen in, 743, 1504.
Knoxvillite, 1407.
Kuromoji oil, 1480.
Kyaphenine, formation and preparation of, 1183.

L.

Lactic acid, action of the bacillus of malignant œdema on, 91.
—— —— formation of, in the organism, 517, 1112.
—— —— inactive, resolution of, by *Penicillium glaucum*, 297.
—— —— resolution of, into its optically active components, TRANS., 754.
Lactocrite, 550.
Lactones, 812, 956.
—— and hydroxy-acids, reciprocal transformations of, 1303.

Lactonic acids, 812, 956.
Lactose, acetyl-derivatives of, 948.
—— optically different modification of, 948.
Lapachic acid, bromo-, Paterno's, TRANS., 638.
—— —— constitution of, TRANS., 611.
Lapachol, constitution of, TRANS., 611.
Lapachone, α-, TRANS., 635.
Lapachone, β-, TRANS., 626.
—— bromo-, TRANS., 638.
Lard, detection of vegetable oils in, 1133.
Lard-oil, iodine number of, by Hubl's method, 664.
Latex of *Ficus carica*, 653.
Lathyrus, analyses of, 522.
Laurel, oil of, 722.
Lauric acid, action of bromine on, 696.
Lautarite, 124.
Lavender, oil of, 868, 1235, 1347.
Lavendol, 868.
Law of Van't Hoff, applicability of Planck's proof to the, 935.
Layers, formation of, in solutions of salts in mixtures of water and organic liquids, 1146.
Lead. action of nitric acid on, 410, 1403.
—— action of nitric oxide on, 1151.
—— and bismuth, separation of, by means of bromine vapour, 540, 549.
—— and silver, separation of, 1522.
—— bromosulphide, 685.
—— chlorosulphide, 685.
—— chromate, 567.
—— —— basic, 567.
—— dioxide, electrical conductivity of, 672.
—— double halogen salts of, 779.
—— electrolytic detection of, 541.
—— estimation of, 539, 1522.
—— hydrogen imidosulphonate, TRANS., 970.
—— imidosulphonate, TRANS., 969.
—— —— five-eighths oxy-, TRANS., 978.
—— —— hemihydroxy-, TRANS., 970.
—— lowering of the freezing point of cadmium by, TRANS., 903.
—— lowering of the freezing point of, when alloyed with other metals, TRANS., 888, 904.
—— magnesium bromide, 566.
—— new oxyiodide of, 1280.
—— nitride, 112.
—— occlusion of hydrogen by, 942.
—— potassium bromide, 779.
—— —— iodide, equilibrium of, with its aqueous solution, 560.
Lead potassium iodides, 779.
—— separation of bismuth from, 385.
—— silver, and zinc, separation of, in galena and blende, 1378.
—— sulphate, analysis of, 1522.
—— —— crystalline, 1399.
—— tin, bismuth, and cadmium, separation of, 754.
—— volumetric estimation of, 1375.
Lead-gold alloy, analysis of, TRANS., 912.
Lead-potassium alloy, 773.
Lead-sodium alloy, 773.
Lead-thallium alloy, analyses of, TRANS., 914.
Leaves, compounds containing chlorophyll in, 746.
—— etiolated, acquisition of green colour and growth of, 520.
—— —— effect of light on, 521.
—— green and etiolated, amount of proteïds in, 520.
—— of the apple tree, analyses of, 1372.
—— young, absence of oxalates in, 651.
Lecture experiment, burning sulphur in oxygen, 679.
—— —— combination of electrolytic gas, 562.
—— —— diffusion of gases, 562.
—— —— dissociation of phosphonium bromide, 401.
—— —— effusion of gases, 1150.
—— —— occlusion of hydrogen by palladium, 563.
—— —— to illustrate the phenomena of coal dust explosions, TRANS., 414.
Leguminosæ, composition of, 521.
—— source of the nitrogen of, 367, 378.
Lemon oil, crystalline products from, 349.
—— —— reaction of, with mercurous salts, 386.
Lemons, Californian, analyses of, 1511.
Lepidone-violet, 499.
—— —— base, 499.
Lettuce, cooked, composition of, TRANS., 227.
—— existence of hyoscyamine in, TRANS., 90.
Leucæmic patients, peptones in the blood and organs of, 519.
Leucite, artificial reproduction of, 1161.
Leucomaïne, a new, 1367.
Level for gas analysis, 400.
Levulinic acid, action of iodic acid on, 1179.

Levulinic acid, condensation of, with aldehydes, 147.
—— —— condensation of, with furfuraldehyde, 442.
—— —— isonitroso-, 1074.
—— —— magnetic rotation of, TRANS., 800.
—— —— phenylhydrazonehydrazide of, 436.
—— oxime, 1202.
Levulinicphenylhydrazoneazobenzene, 436.
Levulose, cane-sugar, and invert-sugar, examination of, 248.
Licareol, 1236.
Licarcone, 1236.
Licari kanali, essential oil of, 1236.
Light, action of, on oxyhydrogen gas, 939.
—— action of, on ruthenium peroxide, 282.
—— action of, on silver chloride, 775; TRANS., 728.
—— effect of, on etiolated leaves, 521.
Light-intensity, measurement of, 253.
Lignin, 802.
Lignite tar, 1075.
Lignocellulose, reaction of, with ferric ferricyanide, 1421.
Lignocelluloses, 693.
—— constitution of, 129.
Lime, action of, as a manure, with especial regard to paddy fields, 93.
—— action of, on heavy loams, 523.
Lime-seed, oil of, 92.
Limettin, TRANS., 344.
—— action of hydrating agents on, TRANS., 351.
—— action of hydriodic acid on, TRANS., 350.
—— dibromo-, TRANS., 348.
—— nitro-, TRANS., 350.
—— oxidation of, TRANS., 346, 349.
—— trichloro-, TRANS., 349.
Limonene nitrosochlorides, 1349.
Limonenenitrolanilide, hydrochloro-, 1349.
Limonenenitrolanilides, 1348.
—— nitroso-, 1348.
Limonenenitrolbenzylamine, hydrochloro, 1349.
Limonene-series, isomerism in the, 1348.
Limonite in Texas, 1405.
Linaloöl, 868, 1347.
Linamarin, 502.
Lindera sericea, oil of, 1480.
Linseed, sugar from, 1293.
Liquids, application of capillary phenomena to the analysis of, 236.
—— calculation of the specific heat of, 2.
Liquids, heat of dissolution of gases in, 1042.
—— mixed, critical temperatures of, 262.
—— molecular weights of, as evinced by their boiling points, 107.
—— organic, as solvents for metallic salts, 558.
—— relations between compressibility and indices of refraction of, 669.
—— specific heat of, at temperatures above the boiling point, 761.
—— temperatures of saturated vapours of various, under the same pressure, 1143.
—— viscosity of, 1143.
Lithium bromate, 1275.
—— chloride, boiling points of solutions of, TRANS., 341.
—— copper chloride, 118.
—— double chlorides of, with metals of the magnesium group, 1275.
—— hypophosphate, 403.
—— nitride, 565.
—— stannibromide, 121.
Liver, horse's, cystin and xanthine in the, 516.
—— iron in the, 1503.
Live-weight, influence of various salts on, 647.
Loam, heavy, fertility of, increased by lime, 523.
Lotus corniculatus and *L. uliginosus*, composition of, 522.
Lubricating oils, rapid determination of the composition of, 665.
Luminosity of coal-gas flames, TRANS., 322.
Lungs, influence of oxygen on the separation of carbonic anhydride in the, 1369.
Lupanine, the alkaloïd of the blue lupine, 223.
Lupeose, 1171.
Lupins, yellow, assimilation of free nitrogen by, 371, 372, 374.
Lupinus albus, alkaloïds of, 892.
Luteocobalt diaminechromium thiocyanate, 1001.
Lutidine, 2 : 6-, action of benzaldehyde on, 1360.
Lutidinic acid, 75.
Lycium barbarum, alkaloïds of, 232.
Lycopodium saururus, alkaloïds from, 894.
Lysine, 1500.

M.

Magdala-red, solutions of, TRANS., 160, 163.

Magnesium acetate, action of magnesium oxide and lead oxide on, 1178.
—— action of chlorine and of bromine on, 118.
—— action of hydrogen peroxide and of water saturated with carbonic anhydride on, 17.
—— action of nitric acid on, 1403.
—— action of, on ammonia, 409.
—— action of, on chlorides, 776.
—— chloride, boiling points of solutions of, Trans., 341.
—— estimation of, in guncotton, 1520.
—— heats of combination of bromine and iodine with, 762.
—— hypophosphate, 404.
—— lead bromide, 566.
—— lowering of the freezing point of lead by, Trans., 904.
—— manganese chloride and bromide, 781.
—— nitride, 409.
—— orthoborate, 404.
—— oxide, action of hydrogen peroxide on, 1278.
—— permolybdate, 1160.
—— stannibromide, 121.
Magnetic rotation of compounds supposed to contain acetyl, or to be of ketonic origin. Trans., 800.
—— —— of dissolved salts, Proc., 1892, 12.
Magnetism and atomic weight, 672.
—— of organic compounds, 672.
Maize, proteïds of, 379, 746, 749.
Maize-fibrin, 749.
Maize-myosin, 747.
Maize-vitellin, 747.
Maleïc acid, complete transformation of fumaric acid into, 1306.
—— —— thermochemistry of, 1041.
—— —— transformation of, into fumaric acid, 297, 1305.
—— anhydride, preparation of, 963.
Malic acid, new synthesis of, 429.
—— —— separation of, from citric, succinic, and tartaric acids, 1531.
—— —— thermochemistry of, 260.
—— diphenylhydrazine, action of carbonyl chloride on, 511.
Malonamide, diamido-, 40.
—— imido-, 40.
Malondianilide, 1072.
Malonic acid, dibromo-, 1140.
—— —— halogen derivatives of, 39.
Maltose, action of alkaline mercuric cyanide on, 1032.
—— estimation of, in beer and beer wort, 248.
—— hydrate, disappearance of the multirotation of, in ammoniacal solution, 1419.
Maltose, thermochemistry of, 764.
Mammals, formation of uric acid in the blood of, 1257.
Mandelamide, 1203.
Mandelic acid and its nitrile, 1088.
—— —— preparation of the amide, anilide, and phenylhydrazide of, 473.
Mandelic-ψ-tropeïne, 891.
Manganese, action of carbonic oxide on, 568.
—— action of nitric acid on, 1403.
—— and zinc, separation of, 384.
—— calcium, and iron, separation of, 916.
—— compounds, 1052.
—— double halogen salts of, 780.
—— estimation of, by the chlorate method, 1132.
—— estimation of, in iron and steel, 816, 1030, 1524.
—— estimation of, in its ores and alloys, 536.
—— estimation of, in slags and ores, 385.
—— hydroxide from the Euganeen, Italy, 689.
—— separation of iron from, 103.
—— separation of nickel and cobalt from, 240.
—— separation of zinc from, 537.
—— sodium metaphosphate, 1053.
—— tetrachloride, 19.
—— —— hypothetical, 687.
Manganese-ores, estimation of cobalt in, 917.
Manganese-spar from Arzberg, 1406.
—— from Scharfenberg, 1406.
Manganic hydrogen pyrophosphate, 1052.
—— potassium pyrophosphate, 1052.
Manganophyll from Harstigen Mine, Sweden, 1411.
Manganous oxide, action of nitric oxide on, 1152.
—— chloride, 780.
Mangostin, 205.
Mannitol, a pure fermentation of, Trans., 254.
—— and boric acid, freezing points of aqueous solutions of, 263.
—— fermentation of, with *Bacillus ethaceticus*, Trans., 432.
—— monosodium, 800.
—— nitrate, action of alkaline solutions on, 692.
—— occurrence of, in the fruit of the cherry laurel, 908.
—— thermochemistry of, 764.
Mannose, detection of, in vegetable products, 250.
Manure, action of lime as a, with especial regard to paddy fields, 93.

Manure, farmyard, fermentations of, 1123.
—— value of animal *débris* as nitrogenous, 96.
Manures, nitrogenous, preservatives for, 378.
Margarin, detection of, in butter, 1034.
—— estimation of fat in, 392.
Martite from Brazil, 1055.
Masrite, Trans., 494.
Masrium, Trans., 494.
Meat, raw and boiled, digestibility of, 1367.
Mechanical theory of heat, recent developments of, 395.
Medicago, analyses of different species of, 522.
Medicagol, 746.
Meionite, Vesuvian, formula of, 417.
Meldomcter, 414.
Melicitose, thermochemistry of, 764.
Melilite, composition of, 1410.
—— formation of, during the burning of Portland cement, 416.
Melilite-bearing rock from Canada, 1058.
Melilotus alba and *M. officinalis*, composition of, 522.
Melitose, thermochemistry of, 764.
Melting point, depression of, by phenol, 556.
—— —— of minerals, determination of, 414.
Melting points of mixtures, 1139.
Membranes, precipitated, permeability of, 1383.
Menthene, 866, 1479.
—— constitution of, 624.
—— nitrosochloride, 1479.
—— preparation of, 623.
Menthodicarboxylic acid, 202.
Menthol and its derivatives, 866.
—— constitution of, 624, 625.
—— conversion of, into cymene, 200.
Menthonaphthene, 866.
Menthone and its derivatives, 867.
Menthyl ethyl ether, 200, 348.
Menthylamine, 500, 723.
Menyanthes trifoliata, constituents of, 1262.
Menyanthin, 1262.
Menyanthol, 1262.
Mercapturic acids, oxidation products of, 1090.
Mercurammonium compounds, 276.
Mercuric cadmium cyanide, Trans., 687.
—— chloride, boiling points of solutions of, Trans., 340.
—— —— solubility of, in various organic liquids, 558.
—— cyanide, action of aluminium and of nickel, &c., on, dissolved in water and in organic solvents, 797.
Mercuric cyanide, action of ammonia on, 575.
—— —— boiling points of solutions of, Trans., 340.
—— disodium imidosulphonate, Trans., 980.
—— fulminate, action of chlorine on, 26.
—— —— constitution of, 25.
—— thiocyanate, double salts of, with other thiocyanates, 10.
—— zinc cyanide, Trans., 666.
Mercurioanilido-compounds, 1448.
Mercuriophenylamine, 1448.
Mercurosammonium compounds, so-called, 685.
Mercurous hypochlorosulphite, 780.
—— nitride, 112.
—— oxide, action of sulphur on, 770.
—— permolybdate, 1160.
—— salts, action of ammonia on, 686.
—— —— action of hydrogen cyanide on, 1416.
Mercury, action of nitric acid on, 1403.
—— adhesion of, to glass in presence of halogens, Trans., 452.
—— compounds of acetylene, Proc, 1892, 110.
—— dihydrogen imidosulphonate, Trans., 977.
—— electrolytic separation of, 239, 541, 920.
—— electrolytic separation of, from copper, 239.
—— electrolytic separation of, from osmium, 920.
—— hydrosulphides, Trans., 123.
—— imidosulphonates, Trans., 976.
—— —— constitution of, Trans., 985.
—— lowering of the freezing point of bismuth by, Trans., 897.
—— lowering of the freezing point of cadmium by, Trans., 903.
—— lowering of the freezing point of lead by, Trans., 910.
—— phosphide, 1398.
—— potassium imidosulphonate, Trans. 976.
—— separation of, from arsenic, phosphoric, and nitric acids, and from chlorine and sodium, 530.
—— sodium imidosulphonates, Trans., 980.
—— sulphide, colloïdal solutions of, Trans., 138.
—— volumetric estimation of, 663; Trans., 364.
Mesaconic acid, conversion of, into its isomerides by soda, 297.
Mesitylene, derivatives of, 329.
—— fluoro-, 968.
—— iodo-, 967.
Mesitylglycollic acid, 329.

Mesitylglycollic chloralide, 329.
Mesitylglyoxylic acid, salts of, 329.
Mesoxaldehyde, symmetrical bisphenylhydrazone of, 162.
Mesoxanilide, 1439.
—— alcoholate, 1439.
—— hydrate, 1440.
—— imidochloride, 1439.
Mesoxanilidephenylhydrazone, 1439.
Mesoxatoluidide hydrate, 1442.
Metabolism of pigs fed on corn cockle, 1018.
Metallic chlorides, action of magnesium on, 777.
—— films, colours and absorption spectra of, 1037.
—— oxides, action of sulphur and water on, 770.
Metals, action of nitric oxide on, 1151, 1390.
—— action of, on salts dissolved in organic liquids, 797.
—— and nitric acid, reaction between, 1402.
—— direct combination of chlorine with, 118, 401.
—— direct combination of chlorine and bromine with, 118.
—— electrical behaviour of, in salt solutions, 393.
—— electrical volatility of, 1037.
—— electrolytic estimation of, 1521.
—— electrolytic estimation of, as amalgams, 753.
—— heavy, volumetric estimation of, 1521.
—— nitro-, 1390.
—— transportation of solids in a vacuum by the vapours of, 1386.
Metapectic acid, 291.
Metaphosphates, 1045.
Meteoric iron, discovery of diamonds in, 284.
—— —— from Colfax Township, North Carolina, 1059.
—— —— from Maryland, 794.
—— —— Welland, kamacite, tænite, and plessite from, 24.
Meteorite from Kansas, 795.
—— of Jelica, 795.
—— of Ljungby, 1060.
—— of Misshof, in Kurland, Russia, 1059.
—— the Tonganoxie, 284.
Meteorites from Atacama, Chili, 1413.
—— new, 1413.
—— of Turgaisk, 418.
Methane, absorption coefficient of, in water and in alcohol, 1044.
—— action of heat on, Trans., 328.
—— flame, experiments on, Trans., 310.
Methane, iodonitro-, preparation of, 1415.
Methaneazobenzene, iodonitro-, 1416.
Methaneazotoluene, iodonitro-, 1416.
Methenylamidoximeacethydroxamic acid, 139.
Methenylnaphthaleneamidine, 1496.
Methoxyacetophenone, ortho-, 845.
Methoxyacetophenonecarboxylic acid, 1231.
Methoxybenzhydrylamine, para-, 338.
Methoxybenzophenone, para-, chloride, 339.
—— —— hydrazones of, 340, 598.
Methoxybenzophenone-β-naphthylamine, para-, 339.
Methoxybenzophenoneparamidobenzoic acid, para-, 340.
Methoxybenzophenoneparatoluidine, para-, 339.
Methoxybenzoylacetic acid, ortho-, 844.
Methoxybenzylideneorthamidophenol, 1451.
Methoxybenzylideneparamidophenol, 1451.
Methoxycresol, 447.
Methoxydiazobenzenesulphonic acid, para-, 1081.
Methoxyethylbenzoic acid, orthochloronitro-, 1231.
Methoxyjulolidine, para-, 1492.
Methoxyorthohydroxyacetophenone, para-, 59.
Methoxyquinine methiodide, 1363.
Methoxyparahydroxybenzophenylhydrazone, ortho-, 317.
Methoxyphenyldimethylpyrazolone, para-, 1082.
Methoxyphenylhydrazine, para-, 1082.
Methoxyphenylhydrazinesulphonic acid, salts of, 1081.
Methoxyphenyloximidoacetic acid, para-, 328.
Methoxyphenylphenylpyrazolone, ortho-, 844.
Methoxypyridine, α-, 209.
Methyl acetoneoxalate, magnetic rotation of, Trans., 822, 853.
—— acetophenoneoxalate, magnetic rotation of, Trans., 833, 863.
—— alcohol, vapour tension of, 397.
—— alloethyl camphorate, ortho-, 1102.
—— α-amidopropionate hydrochloride, 453.
—— apionylglyoxylate, 328.
—— azomethylenecarboxylate, 452.
—— benzeneazocamphocarboxylate, 1344.
—— benzenesulphonate, 1220.
—— bromobenzenesulphonate (para-), 1220.
—— bromotetramethylenecarboxylate, Trans., 43.

Methyl butyl ether, 27.
—— —— ketone, oxidation of, 36.
—— camphocarboxylates, 1342.
—— camphorate, 1346.
—— carboxymethylacetoacetate, 1070.
—— chlorobenzenesulphonate (para-), 1220.
—— cumaroketone (ortho-), 169.
—— α-diazopropionate, 452.
—— dicarboxyglutarate, 1040.
—— —— thermochemistry of, 1041.
—— dioxymethylenephenylglyoxylate, 327.
—— dioxymethylenephenyloximidoacetate, 327.
—— diphenyl tricyanide, formation of, 1184.
—— ethyl ketone, action of chlorine on, 425.
—— —— ketoxime, action of phosphoric chloride on, 426.
—— —— sulphide, preparation of, 1422.
—— hexyl ketone, isonitroso-, 971.
—— —— —— normal, 293.
—— —— ketoxime, 427.
—— hydrogen camphorate, 1346.
—— —— —— allo-, Trans., 1093.
—— —— —— —— crystallography of, Trans., 1094.
—— —— —— ortho-, 1102 ; Trans., 1088.
—— —— —— —— crystallography of, Trans., 1088.
—— —— camphorates, action of phenylcarbimide on, 1347.
—— —— phthalate, dissociation constant of, Trans., 717.
—— —— —— preparation of, 1204.
—— —— succinate, dissociation constant of, Trans., 716.
—— hydroxycinnamyl ketone (ortho-) and its derivatives, 169.
—— α-hydroxypropionate, nitro-derivatives of, 583.
—— imidomethylphenylthiocarbamate, 466.
—— imidophenylthiocarbamate, 465.
—— isoamyl ketone, oxidation of, 36.
—— isobutyl ketone, 36.
—— isopropyl ketoxime, action of phosphoric chloride on, 427.
—— licaryl ether, 1236.
—— mesitylenecarboxylate, 329, 715.
—— methylcamphocarboxylate, 1344.
—— methylimidomethylphenylthiocarbamate, 466.
—— methylphenyldithiocarbamate, 466.
—— methylphenylthiocarbamate, 466.
—— morphine carbonate, 638.
—— α-naphthalenesulphonate, 1220.
—— β-naphthalenesulphonate, 1220.
Methyl naphthyl ketones, action of phosphoric chloride on, 465.
—— β-naphthylsulphinate, 623.
—— naphthylsulphoneformate, 623.
—— opianates, normal and pseudo-, 1209.
—— phenylamidoacetate, 468.
—— phenylcarbamate, nitration of, 711.
—— phenylimidomethylphenylthiocarbamate, 466.
—— phenylmethyltriazolecarboxylate, 638.
—— propyl ether, 27.
—— —— ketone, hepatchloro-, 1463.
—— —— —— hexachloro-, 1462.
—— α-pyridyllactate, 76.
—— salts of abnormal structure, 1208.
—— tetrachloro-α-hydroxyhydrindenecarboxylate, 858.
—— tetrahydroquinolinecarboxylate, 355.
—— trimethylenetetracarboxylate (1 : 1 : 2 : 2-), 1040.
Methylacetylacetone, magnetic rotation of, Trans., 813, 842, 848.
—— refractive and dispersive powers of, Trans., 850, 852.
Methylacetylacetonitrile, 810.
Methylacetylcarbinol, 810.
Methylacetylcarbinyl acetate and butyrate, 810.
Methyl-β-acetylquinoline, α-, 1107.
Methylacridone, 881.
Methylalloxazine, 70.
Methylamidocrotonanilide, 965.
Methylamidocrotonanilide, β-, 708, 1106.
Methylamidoparadiketohexene, pentachloro-, 449.
Methylamine hydrogen diaminechromium thiocyanate, 1000.
—— —— malate, action of heat on, 820.
—— platinothiocyanate, 286.
Methylarecaïdine, 739.
Methylbenzenes, condensation of, with allyl alcohol, 156.
Methylbenzylamine, 65.
Methylbenzylmetaxylidine, 1320.
Methylbenzylorthotoluidine, 313.
Methyl-μ-benzyloxazoline, β-, 214.
Methylbergaptic acid, 71.
Methylbromophenyldibromopyrazolone, 1246.
Methylcamphor, 1343.
Methylcarbazacridine, 343.
Methylchlorostilbene, 1224.
Methyl-μ-cinnamenyloxazoline, β-, 215.
Methylcoumaroxime, α-, 330.
Methylcrotonanilide, β-, derivatives of, 1106.
Methyldeoxybenzoïnorthocarboxylic acid, para-, 473.
Methyldeoxystrychnine, 1014.

Methyldiphenylformamidine, 707.
Methyldipyridyls, 75.
Methyldithiobiuret, α-, 703.
Methylene iodide, action of, on diethyl malonate, 1304.
—— —— action of silver nitrite on, 1415.
—— —— refractive power of, at different temperatures, TRANS., 296.
—— iodo-, reaction of, with silver nitrate, 575.
Methylenecarbazole, 1466.
Methylenecinchonic acid, 1489.
Methylenecinchoxinic acid, 1490.
Methylenediacetamide, 579.
Methylenedibenzamide, 467, 580.
Methylenedigallic acid, 856.
Methylene-3 : 4-dihydroxybenzyl glycol, 47, 310.
Methylenedimetanitraniline, 1450.
Methylenediditrodibenzamide, 467.
Methylenediorthonitraniline, 1450.
Methylenediorthotoluylamide, 467.
Methylenediparanitraniline, 1450.
Methylenediparatoluylamide, 467.
Methylenedipyrogallol, 856.
Methylenediresorcinol, 856.
Methylenediresorcylic acid, 856.
Methylenedisalicylic acid, 855.
—— —— condensation of, with β-resorcylic acid, with gallic acid, and with phenol, 857.
Methylenedithioacetamide, 580.
Methylenedi-α-toluylamide, 467.
Methylenehydroxyquinolinium, 878.
Methylenephthalyl, nitro-, 1231.
Methylethylacraldehyde, action of sulphuric acid on, 951.
Methylethylbenzene, metadiamidopara-, 606.
Methylethylbromazolone, 79.
Methylethylhydroxyquinoline, 79.
Methylethylisoxazole, amido-, 79.
Methylethylpiperidylalkine [2 : 5-], 1358.
Methylethylpyridylalkine [2 : 5-], derivatives of, 1358.
Methylethylsulphine, preparation of, 1522.
Methyleugenol, glycol from, 310.
Methylfenchylamine, 1239.
Methylfumaramic acid, 821.
Methylfumarimide, 821.
Methylfurfurylthiocarbamide, 43.
Methylglutaric acid, β-, 41.
Methylglyoxaline, action of ethyl chloracetate on, 1493.
Methylglyoximecarboxylic acids, dissociation constants of, 1268.
Methylguvacine, 740.
Methylhexahydronicotinic acid, 740.
Methylhexylcarbin cyanide, 132.
Methylhexylethylene, β-, 132.
Methylhydantoïn, γ-, 828.
Methylhydratropic acid, para-, 605.
—— —— —— metadiamido-, 606.
—— —— —— metadinitro-, 606.
Methylhydrazimethylenecarboxylic acid, ammonium salt of, 452.
Methylhydrindone, ortho-, 1221.
—— —— phenylhydrazone, 1221.
Methylhydrobergaptic acid, 72.
Methylhydrocinnamic acid, ortho-, 1221.
—— acids, condensation of, to the corresponding methylhydrindones, 1221.
Methylhydrocotoïn, action of phosphoric chloride on, 1314.
Methylhydrohydrastinine, bromo-, 223.
Methylhydroxy-γ-acetoxime-δ-isonitrosoamidovaleric acid, β-, lactam of, 326.
Methylhydroxy-γ-cyanacetobutyronitrile, β-, 325.
Methylhydroxylamine, 1067.
Methylhydroxyphthalanil, α-, 608.
Methylhydroxyphthalanilic acid, α-, 608.
Methylhydroxypyrimidinecarboxylic acid, 1008.
Methylhydroxytoluquinoxaline, 1359.
Methylindole, α-, action of methyl iodide on, 614.
Methylisobutylthiocarbamide, symmetrical, 702.
Methylisoeugenol, glycol from, 311.
—— nitrosite of, 447.
Methylisoform-α-naphthalide, 705.
Methylisoformoparatoluidide, 708.
Methylisoformortholuidide, 707.
Methylisoglyceric acid, β-, 296.
Methylisoglycidic acid, β-, 296.
Methylisoxazole, α-, 1073.
Methylisoxazole, γ-, 1073.
Methyljulolidine, γ1-, 498.
Methyllepidone, dyes obtained from, 498.
Methylmalic acid, β-, 589, 963.
Methylmalonic acid, thermochemistry of, 1140.
Methylmetanitroformanilide, 706.
Methylmetanitroisoformanilide, 706.
Methyl-μ-metanitrophenyloxazoline, β-, 214.
Methylmethenylnaphthaleneamidine, 1496.
Methylnaphthalene, α-, chloro-, 494.
—— nitro-, 494.
—— trichloro-, 493.
Methylnaphthalene, β-, chloro-, 494.
—— chloro-derivatives of, 493.
Methylnaphthalenes, α- and β-, 492.
—— action of chlorine and of nitric acid on, 493.
Methylnaphthaloxazine, 70.
Methyl-α-naphthindole, 3'-, 1479.

Methylnonylacetylene, 1164.
Methylœnanthaldoxime, 1436.
Methylorthocumaryl alcohol, 169.
Methylorthophenylenediamine, 1475.
Methyloxymethylenetribromopyrogallol, 311.
Methyl-α-oxy-β-methylhydroquinoxaline, meta-, 1359.
Methylparaphenylglycoluric acid, 828.
Methylparethyltoluene, meta-, 985.
Methylpentadecylacetylene, 1163.
Methylphenanthridine, ortho- 198.
Methylphenanthridine, para-, 197.
Methylphenanthroline, 729.
Methylphenyldihydroquinazoline, 81.
Methylphenyldihydroxyglutaric acid, 1471.
Methylphenylenethenylamidine, 1475.
Methylphenylhydrazone, thionyl-, 1324.
Methyl-2′-phenylindole, 1-, 1465.
Methyl-2′-phenylindole, 3-, 1466.
Methylphenylketodihydroquinazoline, 81.
Methylphenylpyrazolone and its derivatives, 1245.
Methylphenylpyrazolonesulphonic acid, 1245.
—— chloride, dichloro-, 1246.
Methylphenyltetrahydroquinazoline, 81.
Methylphthalic acid, 1221.
—— —— α-, 607.
—— anhydride, 1221.
Methylphthalide, dichloronitro-, 1231.
Methylphthalimide, 1221.
—— α-, 607.
Methylphthalodiamide, α-, 607.
Methylpipecolylalkine, 1-, 1245.
Methylpiperidine, β-, derivatives of, 629.
Methylpropylacetic acid, preparation of, from ethyl acetoacetate and from diethyl malonate, 581.
—— —— solubility of salts of, 581.
Methylpropylketoxime, action of phosphoric chloride on, 427.
Methylprotocotoïn, 63.
—— action of phosphoric chloride on, 1314.
Methyl-α-pyridone, 209.
Methyl-γ-pyridone, αββ-trichloro-, 450.
Methyl-γ-pyridonecarboxylic acid, αββ-trichloro-, 450.
Methylpyrrodiazole, 636.
Methylquinidine, 1250.
Methylquinine, preparation of, 222.
Methylquinoline, amidochloro-, 728.
—— quinone oximes, 727, 728, 729.
Methylquinolines, amido-, 727, 728.
—— derivatives of, 726.
—— nitro-, 727, 728.
Methylquinolone, bromo- and nitro-derivatives of, 879, 880, 881.
Methylsaccharin, 1092.
Methylstrychnic acid, 1012.
Methylsuccinic acid, thermochemistry of, 1140.
Methylsulphoneorthamidobenzamide, 335.
Methylsynglyoximecarboxylic acid, 1176.
Methylsynketoximepropionic acid, 1202.
Methyl-Δ^2-tetrahydro-2-hydroxyethylpyridine, 1-, 1244.
Methyltetrahydroketoquinoxaline, 887.
Methyltetrahydroketotoluquinoxaline, 887.
Methyltetrahydronicotinic acid, 740.
Methyl-Δ^2-tetrahydropicoline, 1-, 1243.
Methylthiobiuret, α-, 703.
Methylthiocarbamide, polymeric, 798.
Methylthiocarbimide, compound of, with aldehyde-ammonia, Trans., 517.
Methylthiocoumarin, α-, 329.
Methylthiohydantoïn, 151.
Methylthiophen, dibromo-β-, 830.
—— mercuric chloride, α-, 829.
Methylthiophen-α-carboxylic acid, β-, 830.
Methylthiophensynaldoxime, 1435.
Methyltolualloxazine, 70.
Methyltribromothiophens, oxidation of, 302.
Methyltricarballylic acid, α-, 41.
Methyltricarballylic acid, β-, 42.
Methyltridecylacetylene, 1163.
Methyltrihydroxybenzophenone, 1225.
Methyltropidine, α-, 358.
Methyltropidine, β-, 359.
Methylumbelliferone, derivatives of, 330.
Methylundecylacetylene, 1164.
Methylxanthone, 1092.
Mica, action of water on, 573.
Micas, constitution of, 125.
Microscopic objects, influence of the composition of the glass of slides and cover glasses on the durability of, 1276.
Milarite, 1056.
Milk, action of pilocarpine on the excretion of, 365.
—— analysis, 517.
—— analysis, the Werner-Schmid method of, 390.
—— cause of the rapid curdling of, during thunderstorms, 1370.
—— estimation of fat in, 549, 550, 1134, 1532.
—— estimation of fat in the products from, 391.

Milk, human, analyses of, 517.
—— is alcohol eliminated by the? 365.
—— putrefaction of, 1116.
Milk-solids, extraction of fat from, 391.
Milk-sterilising apparatus, improvements in Soxhlet's, 518.
Mineral springs of Edepsos, 418.
Mineral water. See Water.
Mineralising influence of ammonium sulphate, 1399.
Minerals, determination of the melting point of, 414.
—— from the chrome iron ore deposits of Maryland, 1057.
—— natural classification of, 415.
Mixtures, liquid and gaseous, volumes of, 935.
—— melting points of, 1139.
Molasses, analysis of, 388.
—— preparation of raffinose from, 422.
Molecular compounds, behaviour of, on dissolution, 1154.
—— dissymmetry, 399, 758.
—— volumes of dissolved substances, 1383.
—— weight, diathermanous power, refractive index, and density of a substance, relation between, 1.
—— weights of liquids, as evinced by their boiling points, 107.
—— —— of substances in solution, modification of Beckmann's boiling point, method of determining, Trans., 989.
Molecules, organic, stereochemical models of, 679.
Molybdenite, analysis of, 657.
Molybdenum, action of nitric acid on, 1403.
—— electrolytic separation of gold from, 920.
—— estimation of, 917.
—— fluoroxy-compounds of, 784.
—— sesquioxide, action of nitric oxide on, 1152.
Molybdic acid, action of hydrogen peroxide on, 944.
—— —— colloïdal solutions of, Trans., 155.
—— —— compounds of sorbitol and perseïtol with, 422.
—— —— estimation of, 241.
Moments of inertia, establishment of fundamental formulæ for the calculation of, 948.
Monchiquite, a rock of the elæolite-syenite class, 1058.
Morphine, hydrogen diaminechromium thiocyanate, 1001.
Morphine-violet, 361.
Mucic acid, action of hydrogen phosphide on, 875.
—— —— lactone, reduction of, 825.
—— —— reduction of, 824.
Mucin in myxœdema, 1117.
Multirotation, disappearance of the, of sugars in ammoniacal solution, 1419.
Muscle, frog, Nasse's experiments on the excitability of, in salt solutions, 515.
Muscular work, influence of, on the elimination of creatinine, 364.
Mushrooms, cooked, composition of, Trans., 227.
Mustard oil, estimation of, 1035.
Myristic acid, 311.
—— —— action of bromine on, 696.
—— —— presence of, in ox gall, 1114, 1503.
Myristicinaldehyde, 311.
Myristin and its derivatives, 311.
Mytilus edulis, blood of, 648.
Myxœdema, mucin in, 1117.

N.

Napelline, Trans., 391.
Naphthachloroquinaldine, β-. 1488.
Naphthadihydroxyquinoxaline, 70.
Naphthalaldehydic acid, 864.
Naphthalene, α- and β-bromo-, action of bromine on, Proc., **1891**, 184.
—— chlorobromonitro- [1 : 4 : 2], Trans., 768.
—— constitution of, 69.
—— αβ-diamido-, action of formaldehyde on, 1496.
—— dibromonitro- [1 : 4 : 2], Trans., 769.
—— homonucleal, tri-derivatives of, Trans., 765.
—— α-nitro-, reduction of, 595.
—— nitrobromiodo- [2 : 4 : 1], Trans., 767.
Naphthalenedicarboxylic acid [1 : 2], 1477.
—— —— dioximimide of, 1477.
—— anhydride [1 : 2], 1477.
Naphthalenes, dibromo-, isomeric, the sulphochlorides of, Proc., **1891**, 182.
Naphthalene-series, products of the reduction of alkylated azo-colours of the, 862.
Napthalenesulphonic acid, 1 : 2-amido-, 345.
—— —— 1 : 2 : 2′-α-amidochloro-, 1479.
—— —— 1 : 2′-α-chloro-, 1478.
—— —— 2 : 2′-chloro-, 1478.
—— —— 2 : 4′-β-chloro-, 1478.
—— —— 1 : 3′ : 4-dichloro-, 344.

Naphthalenesulphonic acid, 1 : 2 : 2′-α-nitrochloro-, 1478.
Naphthalenesulphonic acids, chloro-, 1477.
—— —— dibromo-, preparation of ethereal salts of, PROC., **1891**, 184.
Naphthalenesulphonic chloride, α-, 1220.
Naphthalenesulphonic chloride, β-, 1220.
Naphthalide, oxy-, 864.
Naphthaquinone-, β-, action of hypochlorous acid on, 494, 857.
—— nitro-, action of chlorine on, 1229, 1232.
—— sulphonic acids of, 196.
Naphthaphenoquinoxazine, 887.
Naphthaquinone-α-sulphonic acid, β-, sodium salt of, 196.
Naphthenes and their derivatives, 1182, 1311.
—— and polymethylenes, 1310.
Naphthimidine, 983.
Naphthoethylenediamine, β-, 1248.
Naphthoic acid, trichloro-, 493.
Naphthol, α-, 2-amido-, 861.
—— 4-amido-, 861.
—— —— sulphonic acid from, 721.
—— ethyl ether, 4-amido-, 862.
—— 2-nitro-, 861.
—— 2′-nitro-, 1229.
Naphthol, β-, amido-, 862.
—— 1′-amido-, 122, 1234.
—— 4′-amido-, 1233.
—— benzoyl derivative of, 447.
—— chloro-2′-nitro-, 1229.
—— 1′-nitro-, 1234.
—— 2′-nitro-, 1229.
—— 4′-nitro-, 1233.
Naphtholcarboxylic acid, β-, action of aniline on, 1476.
Naphtholdisazobenzeneorthotoluene, α-, 977.
Naphthols, amido-, homonucleal, 861.
—— nitro-β-, 1341.
Naphthol-α-sulphonic acid, α-, 194.
—— —— β-nitroso-, α-, 195.
Naphtholsulphonic acid, 1.4-amido-, 721.
—— —— [1 : 2-], 345.
—— —— β-amido-α-, 477.
Naphtholsulphonic acid, α-amido-β-, 476.
Naphthol-α-sulphonic acid, β-, calcium salt of, physiological action of, 1116.
Naphtholsulphonic acids, amido-, 996.
—— —— nitroso-, 346.
Naphtho-xanthones, 1100.
Naphthoylacetamide, 983.
Naphthyl ethyl ether, 1 : 4-amido-, and its derivatives, 1097.
—— orthotolylcarbamate, 832.
Naphthylacetylene, α-, and its derivatives, 495.
Naphthylacetylene, β-, and its derivatives, 496.
Naphthylamidobiazolone, α-, 510.
Naphthylamidobiazolone, β-, 508.
Naphthylamidosuccinic acid, α-, 860.
Naphthylamidosuccinic acid, β-, 860.
Naphthylamidosuccinic dinaphthylamide, 860.
Naphthylamidothiobiazolone, α-, 511.
Naphthylamidothiobiazolone, β-, 508.
Naphthylamido-ψ-thiobiazolone, α-, 510.
Naphthylamine, bromo- (m. p. 62°), nonexistence of, TRANS., 766.
—— platinothiocyanates, 287.
Naphthylamine, α-, refractive power of, at different temperatures, TRANS., 303.
Naphthylamine, β-, 4 : 1-bromiodo-, TRANS., 767.
—— 1 : 4-chlorobromo-, 768.
—— nitration of, 1232.
—— 2 : 4′-nitro-, 1233.
—— 2 : 1′-nitro-, 1234.
Naphthylamines, α- and β-, action of, on ethyl bromosuccinate, 860.
Naphthylanilidodithiobiazolone, α-, 511.
Naphthylanilidothiobiazolone, α-, 511.
Naphthylanilidothiobiazolone, β-, 508.
Naphthylaspartic acid, α-, 860.
Naphthyldimethylhydroxypyrimidine, 1009.
Naphthylene dihydrosulphides, 1471.
—— dithiocyanate, 1471.
Naphthyleneamidinedimethoxybenzenylorthocarboxylic acid, αβ-, 1249.
Naphthylenediamine, 2 : 1′-, 1234.
Naphthylenediamine, 2 : 4′-, 1233.
Naphthylenedimethoxyphthalamidone, αβ-, 1249.
Naphthylethylene, chlor-α-, 495.
Naphthylethylene, chlor-β-, 495.
Naphthylglycocinenaphthylide, α-, 1341.
Naphthylglycocine-α-naphthylidoacetic acid, α-, 1341.
Naphthylglycocines, derivatives of, 1341.
Naphthylhydrazone, thionyl-α-, 1324.
Naphthylhydroxypyrimidinecarboxylic acid, 1008.
Naphthylidobutyric acid, α-, 1338.
Naphthylidobutyric acid, β-, 1338.
Naphthylidoisobutyric acids, derivatives of, 1342.
Naphthylidopropionic acid, α-, 1337.
Naphthylido-α-propionic acid, β-, 1337.
Naphthylimidazole, να-, 1331.

Naphthylimidazole-μ-mercaptan, $\nu\alpha$-, 1331.
Naphthylimidazolyl-μ-methyl sulphide, $\nu\alpha$-, 1331.
Naphthylmethyl chloride, α-, 494.
Naphthylmethylbiazolone, α-, 509.
Naphthylmethylbiazolone, β-, 508.
Naphthylmethylhydroxypyrimidine, 1009.
Naphthylmethylsulphone, β-, 623.
Naphthylmethyl-ψ-thiobiazolone, α-, 509.
Naphthylmethyl-ψ-thiobiazolone, β-, 508.
Naphthylmethylthiohydantoïn, α-, 150.
Naphthylphenylacetic acid, 1094.
Naphthylphenylacetonitrile, 1094.
Naphthylphenylbiazolone, α-, 509.
Naphthylphenylhydroxypyrimidine, 1009.
Naphthylphenylsemithiocarbazide, α-, 511; Trans., 1019.
Naphthylphenylsemithiocarbazide, β-, Trans., 1020.
Naphthylphenyl-ψ-thiobiazolone, α-, 510.
Naphthylquinoline, 1107.
Naphthylthiocarbamic acids, salts of, 56.
Naphthylthiocarbamide, α-, 1331.
Naphthylthiocarbizine, α-, 510.
Naphthylthiosemicarbazide, α-, 510.
Narcotine, reaction of, 756.
Nascent action, 257.
Natrolite from Magnet Cove, Arkansas, 793.
—— from Monte Baldo, 690.
Neodymium oxide, emission spectrum of, 2.
Nerves, heat production in, during excitation, 365.
Neurine, 219.
—— action of hydriodic and hydrobromic acids on, 808.
—— derivatives of, 806, 905.
Newtonite, 22.
Nickel, action of nitric acid on, 1278.
—— action of nitric oxide on, 1152.
—— ammonium sulphate, 1283.
—— atomic weight of, 1158.
—— carbonyl, oxidation of, 279.
—— —— physiological action of, 365.
—— detection of, 1525.
—— electrolytic separation of cadmium from, 920.
—— fluoride, 1159.
—— fluoroxyhypovanadate, 787.
—— nitrate, basic, 1157.
—— occlusion of hydrogen by, 567.
—— oxide, behaviour of, on strong heating, 1159.
Nickel potassium fluoride, 781.
—— reactions, 1132.
—— salts, action of alkaline polysulphides on, 537.
—— separation of iron from, 103.
—— separation of manganese from, 240.
—— sulphate, anhydrous, 1283.
—— —— —— crystallised, 941.
Nicotenylamidoxime, 206.
—— benzyl ether, 208.
Nicotenylazoximebenzenyl, 207.
Nicotenylazoximepropenyl-ω-carboxylic acid, 207.
Nicotenylazosulphimecarbanilide, 208.
Nicotenylphenyluramidoxime, 208.
Nicotiana tabacum, alkaloïds of, 232.
Nicotine, 1010, 1497.
—— action of bromine on, 1497.
—— action of silver acetate on, 1104.
Nicotinic acid, 3′-bromo-, 876.
Nipecotinic acid and its derivatives, 1485.
Nitramine of the quinoline group, attempted synthesis of, 725.
Nitrates, action of the copper-zinc couple on, in acid solution, 1518.
—— basic, 1157.
—— —— decomposition of, by water, 1272.
—— estimation of, in water, 243.
—— estimation of nitrogen in, 527, 528, 1517.
Nitrate-reducing ferment in straw, 1259.
Nitric acid, action of nascent hydrogen and nascent oxygen on, 680.
—— —— action of, on metals, 1278, 1402.
—— —— and lead, chemical changes between, 410.
—— —— colour of, 113.
—— —— gasometric estimation of, 1375.
—— —— manufacture of, 941.
—— —— reduction of, to ammonia by the galvanic current, 403.
—— —— separation of, from mercury and phosphoric and arsenic acids, 530.
—— —— tables revised, 13.
Nitric oxide, absorption coefficient of, in alcohol, 1044.
—— —— action of, on metallic oxides, 1151, 1271.
—— —— action of, on metals, 1151.
—— —— action of potash on, 940.
—— —— and oxygen, reaction between, 940.
—— —— behaviour of, at high temperatures, 940.
—— —— estimation of free oxygen by means of, 97.

Nitric oxide, preparation of, 939.
Nitric peroxide, action of, on metals and metallic oxides, 1390.
—— —— liquid, dissociation of, Trans., 242.
Nitrification, comparative, of humus and undecomposed organic matter, 906.
—— in organic media of acid reaction, 906.
—— influence of clay and organic nitrogen on, in fallow soils, 656.
—— loss of nitrogen during, 374.
—— of organic nitrogen, 367.
Nitriles, action of sulphuric anhydride on, 713.
—— additive products of, with hydrogen iodide, 1448.
—— aromatic, 344.
—— —— formation of, 1094.
—— dimolecular, 450.
—— ketonic, action of hydroxylamine on, 79.
—— polymerisation of, 576.
—— refractive powers of, 757.
—— unsaturated, synthesis of, 1340.
Nitrites, action of the copper-iron couple on, in acid solution, 1518.
—— in water, influence of temperature on Griess' reaction for, 657.
Nitro-compounds, coloured, constitution of, Proc., **1892**, 101.
—— fatty, 575.
—— first product of the reduction of, 291, 594, 1067.
—— first product of the reduction of, with stannous chloride, 594, 1067.
Nitrogen, absorption coefficient of, in alcohol, 1043.
—— atmospheric, accumulation of, in cultivations of *Bacillus radicicola*, 1019.
—— —— assimilation of, 1507.
—— —— fixation of, by arable soils, 522.
—— Boyer's method of estimating, 1517.
—— compounds, stereochemical isomerism of, 338, 598.
—— —— stereoisomeric, dissociation constants of, 1268.
—— —— —— nomenclature of, 312, 875.
—— direct combination of, with the alkaline earth metals, 566.
—— dissolved in blood, 1257.
—— estimation of, 237, 751. 1125.
—— estimation of, in nitrates, 527, 528, 1517.
—— estimation of, in organic substances, 1516.
—— excretion of, in kidney diseases, 743.
Nitrogen, excretion of, in urine, 1503.
—— for plants, rain as a source of, 233.
—— free, assimilation of, by plants, 367, 370, 378, 523.
—— —— fixation of, by leguminous plants, 369.
—— —— fixation of, by plants, 1021.
—— —— fixation of, during vegetation, 1508.
—— influence of hot baths on the excretion of, from the human system, 1503.
—— influence of water and sodium chloride on the excretion of, 904.
—— loss of, in the decomposition of nitrogenous matters in the soil, 374.
—— of leguminous crops, sources of the, 367.
—— organic, estimation of, 527.
—— —— nitrification of, 367.
—— question, 374.
—— rings containing, nomenclature of, 312, 875.
—— solubility of, in water, 108, 271.
Nitrogen-free extract, constituents of, 653.
Nitro-group, displacement of the, by chlorine or bromine, 305.
—— first reduction products of, 291, 594, 1067.
Nitro-metals, 1390.
Nitrosilicic acid, existence of, 684.
Nitrosoazo-compounds, constitution of, 1321, 1453.
Nitrosulphonic acids, preparation of, 475.
Nitrous acid, detection of, 1124.
—— —— estimation of, 751, 1029.
Nitrous oxide, absorption coefficient of, in water and in alcohol, 1044.
Nomenclature, international system of, Proc., **1892**, 127.
—— of cycloïds, Proc., **1892**, 127.
—— of rings containing two carbon and three nitrogen atoms, 889.
—— of stereoisomeric nitrogen compounds and of rings containing nitrogen, 312, 875.
Nonenylamidoxime, 132.
Nononaphthene, action of nitric acid on, 443.
—— amido-, 443.
—— ketonic compound from, 443.
—— nitro-, 443.
Nonylamine, 132.
—— action of nitrous acid on, 132.
Nonylcarbamide, 132.
Nonyldithiocarbamic acid, 132.
Norhemipinic acid, meta-, 180.
Nucleïc acid and guanine, supposed compound of, 1501.

Nucleïn, 224, 1501.
—— formation of uric acid from, 646.
Nutrition, influence of, on the assimilation of free nitrogen by plants, 371.
—— influence of, on the composition of the blood ash, 225.
—— of green plant cells with formaldehyde, 1259.

O.

Oat, proteïds of the, 1120.
Occlusion of hydrogen by palladium: lecture experiment, 563.
Octahedrite, 1055.
Octopus vulgaris, blood of, 648.
Octyl acetate, secondary, 1162.
—— iodide, refractive power of, at different temperatures, TRANS., 295.
Œnanthaldehyde, action of zinc and ethyl chloracetate on, 1300.
—— condensation of, with aniline, 1194.
Œnanthaldoximes, 1436.
Œnanthantialdoxime, 1436.
Œnocarpol, 874.
Oil, essential, of Angostura bark, 644.
—— —— of *Licari kanali*, 1236.
—— kuromoji, 1480.
—— lard, iodine number of, by Hübl's method, 664.
—— of ants, composition of, 948.
—— of bergamot, 349, 868, 1235.
—— —— stearoptene of, 71.
—— of cassia, estimation of cinnamaldehyde in, 924.
—— of cinnamon, 1509.
—— of cloves, valuation of, 250.
—— of laurel, 722.
—— of lavender, 868, 1235, 1347.
—— of lime seed, 92.
—— of mustard, estimation of, 1035.
—— of peppermint, Russian, 723.
—— of petitgrain, 868.
—— of roses, German and Turkish, 203, 625.
—— sesame, detection of, in olive oil, 1133.
—— volatile, from *Aristolochia reticulata*, 70.
Oils and fats, revision of constants employed in the analysis of, 547.
—— essential, 1347.
—— ethereal, oxygen compounds of, 868.
—— fat, absorption and digestion of, by plants, 1118.
—— fatty and mineral, detection of rosin oil in, 548.
—— lubricating, rapid determination of the composition of, 665.
Oils, mineral, heavy, determination of the flashing point of, 542.
—— of lemon and bergamot, crystalline products from, 349.
—— vegetable, detection of, in lard, 1133.
Olefines, action of fatty acids on, 1162.
Oleïc and elaïdic acids, stereoisomerism of, 812.
Olive oil, detection of sesame oil in, 1133.
Onions, Spanish, cooked, composition of, TRANS., 227.
Ononis arvensis, composition of, 522.
Oölitic iron ore of Lorrain, microscopic structure of, 791.
Opianic acid, 179.
—— —— action of acetone on, 179.
—— —— action of acetophenone on, 179.
—— —— bromo-, 1209.
—— —— oxime of, 180.
—— anhydride, oxime of, heat developed in the isomeric change of the, 459.
—— hydrazobenzene, brom-. 1210.
—— methylphenylhydrazone, brom-, 1210.
—— phenylhydrazide, brom-, 1210.
Opianoximic anhydride, brom-, 1210.
Opium, assay of, 926.
Optical chemistry, application of Ketteler's formulæ to, 253.
Optically active substances, behaviour of, in mixtures of two solvents, 1137.
Oranges, Californian, analyses of, 1511.
Orcinol, compound of, with phenylhydrazine, 49.
Organic compounds, magnetism of, 672.
—— matters in the atmosphere, estimation of, 542.
—— substances, estimation of nitrogen in, 1515, 1516.
Organism, fœtal, iron in the, 1502.
—— formation of glucose and lactic acid in, 517, 1113.
—— formation of sugar in the, when oxygen is deficient, 362.
—— living, action of azoimide on, 90.
Organosols, 775.
Orobus niger, composition of, 522.
Orpiment, analysis of, 657.
—— from the Yellowstone National Park, 283.
Oscine, 1498.
Osmium, electrolytic separation of gold, of cadmium, of silver, and of mercury from, 920.
Osmosis, absorption without, 646.
Osmotic pressure and electrolytic dissociation, theories of, 1143.
—— —— measurement of, 556.
—— —— theory of, 676, 765.

Ox gall, presence of myristic acid in, 1114, 1503.
Oxalates, absence of, in young leaves, 651.
Oxalic acid, formation and physiological significance of, in fungi, 230.
—— chloride, 588.
—— diphenylhydrazide, 981.
Oxal-β-naphthalide, dinitro-, Trans., 466.
Oxalorthotoluidide, dinitro-, Trans., 463.
—— tetranitro-, Trans., 464.
Oxalparatoluidide, tetranitro-, Trans., 465.
Oxalyl-β-naphthylhydrazine, 509.
Oxalylorthamido-α-naphthyl mercaptan, 1079.
Oxalylorthamidophenyl mercaptan, 1079.
Oxamethanetolyloxamide, 603.
Oxamethanetolylurethane, 601.
Oxamidotolylurethane, 601.
Oxanilic acid, dinitro-, Trans., 468.
—— —— nitro-, Trans., 468.
—— —— trinitro-, Trans., 469.
Oxanilide, action of nitric acid on, Trans., 458.
—— and its homologues, preparation of, Trans., 459.
—— hexanitro-, Trans., 462.
—— —— hydrolysis of, Trans., 462.
—— tetranitro-, Trans., 460.
—— —— hydrolysis of, Trans., 461.
Oxazine-dyes, 887.
Oxazole, 313.
Oxazolines, 213.
—— formation of, 1331.
Oxetone, 813.
Oxetonedicarboxylic acid, 813.
Oxidation, physiological, 1018.
—— spontaneous, of humic acid and vegetable soil, 655.
Oxides, metallic, action of boron on, 1154.
—— —— action of nitric oxide on, 1151, 1271.
—— —— action of nitric peroxide on, 1390.
Oximes, 1080.
—— action of, on diazo-compounds, 163, 1079.
—— and the so-called stereochemistry, 50.
—— isomeric, 1083.
—— isomerism of, 291.
—— relations between the constitution, configuration, and chemical behaviour of, 1175.
Oximidoacetic acid, 699.
Oximido-acids, dissociation constants of, 1268.
Oxole, 313.
Oxyacanthine, 641.
Oxyacetoindigotin, 991.
Oxyamidosulphonates, action of alkali on, Trans., 988.
Oxy-α-amyrin, 290.
—— acetate, 290.
Oxyazo-compounds, 974.
Oxycellulose, 827.
Oxychrysanthemine, 85.
Oxydehydracetic acid, 585.
Oxygen, aldehydic and ketonic, estimation of, 546, 1530.
—— and carbonic oxide, influence of steam and other gases on the combustion of, 274.
—— and chlorine, reaction of, with hydrogen, 1147.
—— and hydrogen, admixed, slow combustion of, 938.
—— —— compounds of the elements, correlation of, 1270.
—— and nitric oxide, reaction between, 940.
—— atomic weight of, 1388.
—— combination of hæmoglobin with, 1369.
—— dissolved in water, estimation of, 98; Trans., 310.
—— free, estimation of, by means of nitric oxide, 97.
—— —— Schützenberger's process for the estimation of, 98.
—— influence of, on alcoholic fermentation, Trans., 389.
—— influence of, on the separation of carbonic anhydride in the lungs, 1369.
—— solubility of, in water, 108, 271.
Oxyhæmoglobin crystals, oxygen in, 1017.
—— formation of, from hæmatin and a proteïd, 1017.
—— solutions of, Trans., 158.
Oxy-hydrogen gas, absorption of, by soil, 377.
—— —— action of light on, 939.
—— —— ignition temperature of, 680.
—— —— lecture experiments on the combination of, 562.
Oxymercuric hydrogen imidosulphonate, Trans., 977.
—— sodium imidosulphonate, Trans., 983.
Oxymethylenemethoxybutenylbenzene, 311.
Oxymethylquinolines, nitroso-, 727, 728, 729.

P.

Pæonol, 58.
—— phenylhydrazone, 59.
Pæonoloxime, 59.
Pa'inurus vulgaris, blood of, 648.
Palladious oxide, 572.
Palladium, absorption of oxygen by, 943.
—— action of nitric acid on, 1152.
—— atomic weight of, TRANS., 745.
—— direct oxidation of, 572.
—— lowering of the freezing point of bismuth by, TRANS., 894.
—— lowering of the freezing point of cadmium by, TRANS., 900.
—— lowering of the freezing point of lead by, TRANS., 906.
—— occlusion of hydrogen by, 567.
—— occlusion of hydrogen by: lecture experiment, 563.
—— nitrogen compounds, 1284.
Pallasites, the prehistoric and Kiowa Co., 1059.
Palmitic acid, action of bromine on, 696.
Pancreas extract, presence of pentamethylenediamine in, 1368.
Paper, drawing, the acid action of, PROC., **1892**, 19, 34.
—— wall-, estimation of arsenic in, 382.
Paracoto bark, constituents of, 62, 873.
Paraffin-derivatives, boiling points of, 797.
Paraffins, normal, boiling point curves for, 947.
Paraldehyde, condensation of, with chloral, 694.
Paramelaconite, 415.
Paranthracene, 347.
Parapectic acid, 291.
Parapropaldehyde, 1300.
Parsnips, cooked, composition of, TRANS., 227.
Pea-nut, 1122.
Peas, assimilation of free nitrogen by, 371, 372, 374, 378.
—— cooked, composition of, TRANS., 227.
Pectic acid, so-called artificial, from fir-wood, 827.
Pectin-substances, 291.
Pedetic motion in relation to colloïdal solutions, PROC., **1892**, 17.
Penicillium glaucum, action of, on fumarates and maleates, 820.
—— —— resolution of inactive lactic acid by, 297.
Pentabenzoylglucosamine, 134.
Pentacetylxylitol, 29.
Pentadecylacridine, 343.
Pentahydroxyaurindicarboxylic acid, 1469.
Pentahydroxypimelic acid, 1169.
Pentamethylbenzene, chloro-, 968.
Pentamethyldihydroquinoline, 615.
Pentamethylene glycol and its oxides, 1292.
Pentamethylenediamine, 1368.
—— hydrogen diaminechromium thiocyanate, 1001.
—— platinothiocyanate, 287.
Pentamethylenedicarboxylic acid, β-, dissociation constant of, TRANS., 706.
Pentamethylenedicarboxylic acid [1 : 2], melting point of, 1040.
—— —— thermochemistry of, 1041.
Pentamethylethyltrimethylenetrisulphone, 593.
Pentamethyltetrahydroquinoline, 615.
Pentane flame, experiments on, TRANS., 210.
Penterythritol, 127.
—— thermochemistry of, 764.
Pentethylphloroglucinol, bisecondary, oxidation of, 1188.
Pentonic acid, new, 437.
Pentosans of woody vegetable fibre, 1420.
Pentose carbohydrates, digestibility of, 645.
Pentoses, detection of, in vegetable products, 250.
—— estimation of 247, 388.
—— physiological action of, 1506.
Pentoxazolines, 213.
Peppermint oil, Russian, 723.
Peptone, decomposition of, in the human body, 904.
—— salts from glutin, 895, 1016.
Peptones, analysis of, 1535.
—— constitution of, 1499.
—— estimation of, in stomach contents, 1136.
—— formation of sugar from, in blood, 1502.
—— in the blood and organs of leucæmic patients, 519.
—— molecular weights of, 1501.
—— salicylsulphonic acid as a test for, 552.
—— volumetric estimation of, in urine, 1264.
Peridotite in Central New York, 1057.
Periodic relations of the elements, 562.
Permanganate solutions, stability o 1524.
Permanganates and hydrogen peroxide, reaction between, 277.

Permeability of precipitated membranes, 1383.
Permolybdates, 1160.
Permolybdic acid, 1283.
—— —— heat of formation of, 1383.
Perruthenates, action of heat on, 282.
Perseïtol, compounds of, with molybdic acid, 422.
—— hydrocarbon derived from, 1065.
—— rotatory power of compounds of, with sodium hydrogen and ammonium hydrogen molybdate, 800.
—— thermochemistry of, 764.
Persulphates, 12.
Persulphuric acid and its salts, 931.
Petalite from Maine, 1411.
Petitgrain, oil of, 868.
Petroleum, pyridine-like bases in, 1357.
Phanerogams, assimilation of free nitrogen by, 370.
Phenacetin, detection of, in urine, 665.
—— orthonitro-, 160.
Phenacetyl-$\alpha\beta$-diphenylacrylamide, β-, 483.
Phenacetyl-$\alpha\beta$-diphenylacrylethylamide, β-, 484.
Phenanthrene and picric acid, solubility relations of the compound of, 1384.
Phenanthridine, 196.
—— methohydroxide, 197.
Phenetoïl, dibromonitro-, 1182.
—— paramido-, oxidation products of, 158.
—— sulphonic acids derived from, Proc., **1892**, 90.
Phenetidine, para-, oxidation products of, 158.
—— —— orthonitro-, 160.
Phenol, action of phospham on, 1311.
—— alkalimetric estimation of, 543.
—— depression of the melting point by, 556.
—— dinitrosonitro-, 594.
—— diorthochloroparabromo-, Trans., 560.
—— metabromonitro-, reduction of, 704.
—— metachlorothio-, 306.
—— orthochlorothio- 308.
—— parachlorothio-, 308.
—— thermal function of, 1042.
—— thermochemistry of, 764, 1042.
Phenoldisazobenzene, constitution of, 976.
Phenoldisazo-orthobenzeneparatoluene, 976.
Phenoldisazoparabenzeneorthotoluene, 976.
Phenoldisazotoluene, 976.
Phenolic acids, instability of carboxyl in, 1332.
Phenolphthaleïn ethyl ether, 1096.
Phenolphthalin ethyl ether, 1319.
Phenols, action of chlorine on, 1186.
—— action of methylchloroform and ethylchloroform on alkaline solutions of, 308.
—— action of phenylhydrazine on, 49.
—— amido-, condensation products of, 1451.
—— and unsaturated hydrocarbons, condensation of, 446, 1443.
—— condensation of, with isoamylene and cinnamene, 447.
—— estimation of, in human urine, 544.
—— isomeric change in the synthesis of, 44.
—— polyhydric, action of dinitrochlorobenzene on, 210.
—— thermochemistry of, 763.
Phenonaphthacridone, 1477.
Phenonaphtho-xanthone, 1099.
Phenoparatolyldihydrotriazine, β-, 734.
Phenophenyldihydrotriazine, γ-, 734.
Phenoquinolino-xanthone, 1099.
Phenoquinoxazine, 887.
Phenoquinoxazone, 887.
Phenotriazines, synthesis of, 734.
Phenoxyamylamine, ϵ-, 717.
Phenoxybutylamine, γ-, 131.
Phenoxybutyronitrile, γ-, 131.
Phenoxypropylmalonic acid, 717.
Phenoxyvaleric acid, γ-, 717.
Phenoxyvaleronitrile, γ-, 717.
Phenyl bromide, refractive power of, at different temperatures, Trans., 299.
—— chloride, refractive power of, at different temperatures, Trans., 298.
—— dithiocarbonate, chloro-, 306, 307.
—— —— parachloro-, 307.
—— dithiocarbonates, 306.
—— iodide, refractive power of, at different temperatures, Trans., 300.
—— isocyanide, preparation and properties of, 1438.
—— α-naphthyl ketone, sodium derivative of, 170.
—— orthacetate, 308.
—— orthomethoxytolyl ketone, 446.
—— phenyl-β-naphthylcarbamate, 166.
—— sodium sulphite, 970, 1076.
—— —— —— action of iodoform on, 1076.
—— thiodi-β-naphthylcarbamate, 166.
—— thiodiphenylcarbamate, 164.
—— xanthate, chloro-, 308.
Phenylacetaldoxime, 1174.
Phenylacetic acid, preparation of, 344.
—— diphenylhydrazide, 981.
Phenylacetometachloranilide, 1465.
Phenylacetoparatoluidide, 1465.
Phenylacetorthotoluidide, 1465.
Phenyl-α-acetoxycrotonic acid, γ-, 472.

Phenylacetylene, silver derivative of, 831.
Phenylacridine, ammonium bases of, 1095.
—— diamido-, preparation of, 1095.
Phenylacridinemethylium ethoxide, 881.
—— hydroxide, 881.
Phenyl-β-alanine, 1342.
Phenylamidoacetic acid, derivatives of, 467.
—— anhydride, 468.
Phenylamidomesoxalic chloride, 1439.
Phenylamidophenylinduline, 342.
—— amido-, 342.
Phenylamines, substituted, action of silicon tetrachloride on, Trans., 453.
Phenylamphiglyoxime, anti-, 321.
Phenylamphiglyoximecarboxylic acid, 1177.
Phenylangelicalactone, 987.
Phenyl-α-anilidocrotononitrile, 1194.
Phenylanthracene, preparation of, 722.
Phenylanthranilic acid, 1086.
Phenylantiglyoxime, 321.
Phenylazimidobenzene, 889.
—— amido-, 1322.
—— tetranitro-, 1454.
Phenylazorthohydroxymethylquinoline, meta-, 506.
Phenylazoxazole, 322.
Phenylazoxazolecarboxylic acid, 1178.
Phenylazoximidobenzene, tetranitro-, 1454.
Phenylbenzenylamidine, 51.
Phenylbenzenylnaphthylenediamine, 1472.
Phenylbenzimidoethyl ether, 52.
Phenylbenzophenone, para-, derivatives of, 186.
Phenylbenzophenoneoxime, para-, 186.
Phenylbenzophenonephenylhydrazone, para-, 186.
Phenylbenzoylbromomethylpyrazolone [1 : 2 : 4 : 3-], 146.
Phenylbenzoyldimethylpyrazolone, 146.
Phenylbenzoylmethylpyrazolone, [1 : 2 : 3-], 146.
Phenylbenzylformamidine, 708.
Phenyl-4-benzylidene-3 : 5-pyrazolidone, 1-, 1005.
Phenylbenzylparatolylcarbamide, 1083.
Phenylbenzylthiourea, unsymmetrical, Proc., 1892, 97.
Phenylbromobutyrolactone, 987.
Phenylbromodihydroxybutyrolactone, 1447.
Phenyl-γ-bromo-α-hydroxybutyric acid, γ-, 471.
Phenylbromohydroxycrotonic acid, 1447.
Phenylbromotrimethylene-ψ-thiourea, n-, Trans., 550.
Phenyl-γ-bromovaleric acid, 988.
Phenylbromovalerolactone, 987.
Phenylcarbamide and its derivatives, 480.
—— bromo-derivatives of, 467.
Phenylchloracetonitrile, 1088.
Phenylcinnamonitrile, 344.
Phenylcroton-α-lactone, γ-, 472.
Phenyldibenzoylmethylpyrazolone [1 : 2 : 4 : 3-], 146.
Phenyl-2 : 4-dibenzoyl-3 : 5-pyrazolidone, 1-, 1005.
Phenyldibenzylcarbamide, 1083.
Phenyldibromobutyric acid, decomposition of, 987.
Phenyldibromohydroxybutyronitrile, 1447.
Phenyldibromovaleric acid, decomposition of, 987.
Phenyldifurylnaphthodihydroquinoxaline, 1475.
Phenyldihydroxybutyric acid, 986.
Phenyl-αγ-dihydroxybutyrolactone, γ-, 472.
Phenyldihydroxyvaleric acid, 986.
Phenyldimethylisopyrazolone, 635.
Phenyldimethylpyrazolidone, 731.
Phenyldimethylthiohydantoïn, 150.
Phenyl-β-dimethyl-μ-thiomethylimidazole, ν-, 153.
Phenyldimethylthiourea, Trans., 539.
Phenyldiorthocresolmethane, meta-nitro-, 621.
Phenyldithiobiuret, α-, 704, 844.
Phenyldithiocarbamic . thioanhydride, 55.
Phenyldithiodimethylketuret, α-, 844.
Phenylene hydrogen antimonite, ortho-, 1078.
—— orthotolylcarbamate, meta-, 832.
—— oxide, 1187.
Phenylenediamine, meta-, preservation of solutions of, and its use as a reagent, 1124.
Phenylenediamine, ortho-, action of formaldehyde on, 1496.
Phenylenediphenylpropionic acid, 1228.
Phenylenehydroxylamine, dinitro-, 594.
Phenylethenylamidoximebenzenesulphone, 461.
Phenylethenyldiamidoacetone, 952.
Phenylethyltriazolecarboxylic acid, 637.
Phenylfurazan, 322.
Phenylfurfurylcarbamide, 43.
Phenylfurfurylthiocarbamide, 43.
Phenylglyceric acid, 986.
Phenylglycocine, derivatives of, 1333.
Phenylglycollic acid, action of nitric acid on, 607.
—— —— orthoparadinitro-, 1333.

Phenylglyoximes, 321.
Phenylguanazole, 356.
Phenylguanidine picrate, 950.
Phenylgulosazone, 1-, 823.
—— parabromo-, 823.
Phenylhexyltriazolecarboxylic acid, 597.
Phenylhippuric acid, 468.
Phenylhydantoïn, γ-, 828.
Phenylhydrazidobutyramide, α-, 1192.
Phenylhydrazidopropionic acid, α-, 1196, 1456.
—— nitrile, 1195.
Phenylhydrazimethylenecarboxylic acid, ammonium salt of, 453.
Phenylhydrazine acetate, 981.
—— action of arsenic chloride on, 1326.
—— action of boron chloride on, 1326.
—— action of copper sulphate on hot acid solutions of, 842.
—— action of cyanogen chloride on, 1323.
—— action of, on carbamide, 1323.
—— action of orthonitrobenzyl chloride on, 1455.
—— action of phosphorus trichloride on, 1324.
—— action of silicon chloride on, 1326.
—— carbonyl chloroplatinite, 353.
—— derivatives of, 453.
—— hydrogen diaminechromium thiocyanate, 1001.
—— inorganic derivatives of, 1324.
—— metachloro-, and its derivatives, 454.
—— metallic derivatives of, 1454.
—— oxidation of, with Fehling's solution, 1322.
—— parahydroxyalkyl derivatives of, 1198.
—— paralkyloxy-derivatives of, 1080.
—— parathio-, 1326.
—— paratolylphosphenite, 1325.
—— phosphenite, 1325.
—— phosphite, 1325.
—— thionylthio-, 1326.
Phenylhydrazinebutyric acid, asymmetrical, 635.
Phenylhydrazolepidine, 2-, 1488.
Phenylhydrindone, 1220, 1228.
Phenylhydrocinnamic acid, α-, 1211.
Phenylhydroxyacetonitrile, acetyl derivative of, 1088.
Phenylhydroxybenzenylnaphthylenediamine, 1472.
Phenylhydroxybutyrolactone, 986.
Phenyl-α-hydroxybutyro-γ-lactone, γ-, 472.
Phenyl-α-hydroxycrotonic acid, 471.
Phenylhydroxyformamidine, 708.
Phenylhydroxyphenylethane, 443.
Phenyl-γ-hydroxyvaleric acid, 988.
Phenylhydroxyvalerolactone, 986.
Phenylimidocarbonyl chloride, 1431.
Phenylimidodiacetic anhydride, 1334.
Phenylimidoformic chloride hydrochloride, 1440.
Phenylimidopyruvic chloride, 1440.
Phenylindole, 2′-, 1465.
—— chloro-2′-, 1466.
Phenylinduline, action of acetic acid on, 341.
—— amido-, action of sulphuric acid on, 341.
Phenylisobromobutyrolactone, 987.
Phenylisocrotonic acid, 850.
—— —— oxidation of, 986.
Phenylisodihydroxybutyric acid, 1448.
—— —— salts of, 987.
Phenylisohydroxybutyrolactone, 987.
Phenyl-4-isonitroso-3 : 5-pyrazolidone, 1-, 1005.
Phenylisopropylbenzenylnaphthylenediamine, 1473.
Phenyl-4-isopropylene-3 : 5-pyrazolidone, 1-, 1005.
Phenylisopropyltriazolecarboxylic acid, 638.
Phenylisoxazolone, 1177.
Phenylketodihydroquinazoline, 81.
Phenylketodihydroquinazolinecarboxylic acid, 81.
Phenylketohydroxybutyric acid, 1448.
Phenyllevulinic acid, 988.
Phenyllupetidinedicarboxylic acid, 1487.
Phenyllutidinedicarboxylic acid, 1486.
Phenylmetachlorazobenzene, nitro- and nitronitroso-derivatives of, 454.
Phenylmetachlorazoxybenzene, nitronitroso-, 455.
Phenylmetachlorophenylhydrazine, orthoparadinitro-, 454.
Phenylmetahydroxytolylethane, 446.
Phenylmetamethoxytolylethane, 446.
Phenylmetanitrobenzenylamidine, 52.
Phenylmetanitrobenzenylnaphthalenediamine, 1473.
Phenylmetanitrobenzimido ether, 52.
Phenylmethaneazobenzene, orthonitro-, 1456.
Phenyl-α-methoxy-β-methyl-μ-thiomethylimidazole, ν-, 152.
Phenylmethylbenzoylpyrazolone [1 : 3 : 4-], 146
Phenylmethylenehydrazine, 456.
Phenylmethylethylpyrazole platinochloride [1 : 4 : 5-], 885.
Phenylmethylhydroisopyrazolone, 635.
Phenylmethylisopyrazolone, 635.
Phenylmethylmethylenehydrazine, 457.
Phenylmethylphenylazimethylene, 457.

Phenylmethylpyrazolidone, 731.
Phenylmethylpyrazolone, constitution of, 634.
—— mono-, di-, and tri-bromo-, 731.
—— nitro-, 731.
Phenylmethylthiohydantoïn, 150.
Phenylnaphthostilborosindone, 1247.
Phenylnaphthylenediamine, ortho-, action of benzaldehyde on, 1472.
—— —— action of salicylaldehyde on, 1472.
Phenyl-α-naphthylformamidine, 706.
Phenyl-α-naphthylglycollic acid, 170.
Phenyl-β-naphthylsemithiocarbazide, Trans., 1020.
Phenyl-β-naphthylthiocarbamide, 984.
Phenyl-β-naphthylthiosemicarbazide, 508.
Phenylnonylcarbamide, 132.
Phenylnonylthiocarbamide, 133.
Phenylorthohydroxytolylethane, 446.
Phenylorthomethoxytolylethane, 446.
Phenylorthonitrobenzenylnaphthylenediamine, 1473.
Phenyl-3 : 6-orthopiperazone, 1-, 1494.
Phenyloxazoline, μ-metanitro-, 213.
—— preparation of, 1332.
Phenyloximidoacetonitrile, 322.
Phenylparaditolylcarbamide, 1083.
Phenylparanitrobenzenylnaphthalenediamine, 1473.
Phenylparaphenylglycoluric acid, 828.
Phenylparatolylthiosemicarbazide, Trans., 1014.
Phenylpentoxazoline, μ-, 212.
—— μ-metanitro-, 214.
Phenylpentriazole, meso-, 889.
Phenylphthalimide, preparation of, 1204.
Phenylpiperazine, paranitro-, 210.
Phenylpropiolic acid dichloride, 1464.
—— —— formation of allocinnamic acid from, 848.
Phenylpropionic acid, formation of a hydrocarbon, $C_{18}H_{12}$, from, Proc., 1892, 107.
Phenylpropylamine, 845.
Phenylpropyltriazolecarboxylic acid, 638.
Phenylpyrazolidine, 355.
Phenyl-3 : 5-pyrazolidone, 1-, 1004.
Phenyl-3 : 5-pyrazolidone-4 azobenzene, 1-, 1005.
Phenylpyrazolone, 799.
Phenylpyrazolonecarboxylic acid [1 : 5 : 4], Trans., 797, 799.
Phenylpyridone, αββ-trichloro-γ-, 448.
Phenyl-γ-pyridonecarboxylic acid, αββ-trichloro-, 448.
Phenylpyrrodiazolecarboxylic acid, 1 : 3-, synthesis of, 636.
Phenylquinoline, α-, derivatives of, 1003.
Phenylsantoninmethane, metanitro-, 622.
Phenylsemicarbazide, 1323.
Phenylsuccinamidine, 702.
Phenylsuccinimide, preparation of, 1204.
Phenylsulphone-δ-amidovaleric acid, 354.
Phenylsulphonehydroxypropionic acid, parachloro-, 1091.
Phenylsulphonepropionic acid, α-amido-, 1091.
Phenylsulphonetetrahydroquinoline, 355.
Phenylsynglyoxime, 322.
Phenylsynglyoximecarboxylic acid, 1177.
Phenyltetrahydroketoquinazoline, 1495.
Phenyltetrahydroketoquinoxaline, 886.
Phenyltetrahydroketotoluquinoxaline, 886.
Phenyl-Δ²-tetrahydro-2-methylpyridine, 1-, 1244.
Phenyl-Δ²-tetrahydropicoline, 1-, 1244.
Phenyltetrahydrothioquinazoline, 1495.
Phenyltetrazolecarboxylic acid, amido-, 1009.
—— —— nitro-, 1009.
Phenyltetrazolecarboxylthiamide, 638.
Phenyltetrose, 1447.
Phenylthiocarbamide, 465.
Phenylthiocarbamides, thio-, melting points of, 324.
Phenylthiocarbamineisobutylcyamide, 703.
Phenylthiocarbimide, action of dimethylaniline on, Trans., 538.
—— and chloral-ammonia, Trans., 529.
—— compound of, with aldehyde-ammonia, action of silver nitrate on the, Trans., 518.
Phenylthiocarbimide-aldehyde-ammonia, Trans., 521.
Phenylthiourethane, 600.
Phenyltoluene, meta-, 851.
Phenyltriazolecarboxylic acid, amido-, 735.
—— —— nitro-, 735.
Phenyltrihydroxybutyric acid, 1447.
Phenyltrihydroxybutyrolactone, 1447.
Phenyltrimethylenecarboxylic acids, 849.
Phenyltrimethylene-2 : 3-dicarboxylic acid, Γα1-, 849.
Phenyltrimethylene-2 : 2 : 3-tricarboxylic acid, Γα1-, 849.
Phenyltrimethylmethane, paramido-, 44.
Phenyltrimethylphenylacetonitrile, 1094.

Phenyltri-β-naphthylcarbamide, 167.
Phenylumbelliferone, reduction of, 1228.
Phenyluranilidacetic acid, 468.
Phenylurazole, preparation of, 966.
Phenylvalerolactone, 988.
Phloroglucinol, presence and function of, in plants, 1120.
Phœnicrocoïte, synthesis of, 792.
Pholidolite, 1408.
Phosphamide, 1152.
Phosphates, analysis of, 99, 912.
—— estimation of, 1125.
—— estimation of calcium in, 534.
—— estimation of iron and aluminium in, 536.
—— natural, fluorine in, 1055.
Phosphenylbenzylphenylhydrazone, 1325.
Phosphenylparatolylhydrazone, 1325.
Phosphenylphenylhydrazine, 1325.
Phosphines, tertiary, action of benzal chloride on, 984.
Phosphinobenzene, 1084.
Phosphino-compounds, 1084.
Phosphino-ψ-cumene, 1085.
Phosphinoparatoluene, 1085.
Phosphonium bromide, dissociation of, 401.
Phosphopalladious compounds, 1285.
Phosphoric acid, assimilation of, by crops from the soil, 233.
—— —— basicity of, 394.
—— —— estimation of, by the molybdate process, 1519.
—— —— estimation of, in fertilisers containing cotton seed meal, 1029.
—— —— estimation of, in manures, 1125.
—— —— estimation of, in slags, 382.
—— —— estimation of, in soil, 750.
—— —— estimation of iron and aluminium in the presence of, 755.
—— —— in soil, 750.
—— —— in urine, 1115.
—— —— reverted, estimation of, 1126.
—— —— separation of, from mercury, sodium, chlorine, and from nitric acid, 530.
—— —— volumetric estimation of, 912.
Phosphorous acid, dihydrazide of, 1325.
Phosphorus, allotropic states of, 405.
—— analysis of a slag from the manufacture of, in electrical furnaces, 1401.
—— and sulphur, compounds of, 14.
—— bromonitride, 1272.
—— chloronitride, 1152, 1172.
—— compounds, organic, 875.
—— dilatation of, and its change of volume at the melting point, 7.
Phosphorus, estimation of, in iron, steel, and iron ores, 528, 529.
—— estimation of, in pig iron, 912.
—— poisoning, the urine in a case of, 650.
—— precipitation of, from solutions of iron and steel, 911.
—— trifluoride, action of fluorine on, 12.
Phosphorylphenylhydrazide, 1325.
—— thio-, 1326.
Phosphoryltolylhydrazide, 1325.
Phosphotungstic acids, 1160.
Photometry, colour-, Proc., **1891**, 150.
Phthalamidones, 1248.
Phthalic acid, reduction products of, 1211.
Physical phenomena at very low temperatures, 1138.
Physiological action and chemical constitution of aromatic compounds, relation between, 366.
—— —— of calcium β-naphthol-α-sulphonate, 1116.
—— —— of camphors and of their compounds with chloral, 227.
—— —— of choline, neurine, and allied compounds, 905.
—— —— of dinitrobenzene, 366.
—— —— of gallic and tannic acids, 904.
—— —— of impure chloroform, 745.
—— —— of ketones and acetoximes, 1506.
—— —— of nickel carbon oxide, 365.
—— —— of pentoses, 1506.
—— —— of quinone and quinone derivatives, 1115.
—— —— of sulphonal, 1507.
—— —— of sulphones, 153.
—— —— of strontium salts, 227.
—— —— of triazobenzene, benzamide, α-acetonaphthalide, and ethyl α-naphthylazoacetoacetate, 366.
—— —— of trimethylamine, 366.
Physiological oxidation, 1018.
Phytosterin, 1294.
Picea vulgaris, resin from, 205.
Picene, 623.
Picoline, α-, preparation of α- and β-pyridylactic acids from, 75.
—— dichloro-, Trans., 725.
—— hydrogen diaminechromium thiocyanate, 1001.
Picric acid, bromination of, 156.
Picroaconitine, 1254.
Picrotin, action of hydriodic acid and phosphorus on, 349.
Picrotoxic acid, 349.
Picrylmetachlorazobenzene, 454.
Picrylmetachlorophenylhydrazine, 454.
Pigs fed on corn cockle, metabolism in, 1018.

Pillijanine, 894.
Pilocarpine, action of, on the excretion of milk, 365.
—— hydrogen diaminechromium thiocyanate, 1901.
Pimelic acid, derivatives of, 428.
—— —— dissociation constant of, Trans., 700.
—— —— thermochemistry of, 1041.
—— anhydride, dihydrazido-, 435.
Pinacone, thio-, 1317.
Pineapple juice, ferments in, 650.
Pinene, constitution of, 865, 997.
Pinenenitrolallylamine, 998.
Pinenenitrolamylamine, 998.
Pinenenitrolbenzylamine, 998.
Pinenenitrolpropylamine, 998.
Pinna squamosa, ash of the blood of, 1016.
—— —— blood of, 649.
Pinnaglobin, a new globulin, 1016.
Pinone glycol and its derivatives, 998.
Pinus abies, terpenes from the resin of, 625.
—— *laricio*, resin from, 204.
—— *sylvestris*, pollen of, 232.
Pinylamine, 996.
Pinylcarbamide, 997.
Piperazine, 210.
—— dichloro-, 211.
Piperidine and furfuraldehyde, condensation of, 1452.
—— argento-salts, 1483.
—— chloricdide, 1357.
—— derivatives of, oxidation of, 354.
—— oxidation of, 1104.
—— oxidation of, by hydrogen peroxide, 1484.
—— synthesis of, 717.
—— thiocyanate, 1110.
Piperidine-bases of the β-series, 628.
Piperidinecarboxylic acids, 1486.
Piperonalamidoxime, 318.
Piperonaldoxime, 318.
Piperonalonitrile, 318.
Piperylacetoguanamine, 736.
Piperylbiguanide, 735
Piperylformoguanamine, 735.
Pipette for weighing fuming liquids, 13.
—— gas-, improved, 1374.
—— improved for gas absorptions, 1124.
Pisum arvense, composition of, 522.
Plant food, sodium as a, 1508.
Plant-cells, green, nutrition of, with formaldehyde, 1259.
Plants, absorption and digestion of fat oils by, 1118.
—— assimilation of free nitrogen by, 367. 370, 378, 523.
—— direct absorption of ammoniacal salts by, 229.
Plants, fat-decomposing ferments in, 1261.
—— fixation of free nitrogen by, 1021.
—— gum in, which yields xylose on saccharification, 1371.
—— influence of carbohydrates on the accumulation of asparagine in, 91.
—— occurrence of guanidine in, 908.
—— presence and function of phloroglucinol in, 1120.
—— respiration of, when injured under lessened oxygen tension, 1259.
—— sodium chloride in, 651.
Plasma and serum, 1113.
Platinic bromide and its compounds, heat of formation of, 3.
—— chloride, testing the purity of, 1526.
Platinoselenostannates, 282.
Platinothiocyanates, 286.
—— of the alkaloïds and amines, 287.
Platinous chloride, Trans., 445.
—— —— use of, as a source of chlorine, Trans., 445.
Platinum, absorption of oxygen by, 943.
—— iodonitro- and bromonitro-compounds of, 280.
—— lowering of the freezing point of bismuth by, Trans., 896.
—— lowering of the freezing point of cadmium by, Trans., 901.
—— lowering of the freezing point of lead by, Trans., 909.
—— nitrogen compounds of, 1283.
—— occlusion of hydrogen by, 567.
—— pure, preparation and assaying of, 789.
—— tetrachloride, anhydrous, Trans., 422.
—— thiocyanate, 286.
Platodipyridine bromide, 353.
—— chloride, 352.
Platosemipyridine chloride, 352.
Platosopyridine chloride, 352.
—— dibromide, 353.
Plessite from the Welland meteoric iron, 24.
Pneumonia, ptomaïne of, 1258.
Poisons, vegetable, influence of, on the germination of seeds, 228.
Polarisation, galvanic, at small electrodes, 759.
Pollen of *Pinus sylvestris*, 232.
Polydymite, 124.
Polymethylenes and naphthenes, 1310.
Polythionates, Proc., 1892, 91.
Potassammonium, reaction of, on metals, 275.
Potassium acetate solutions, electrolysis of, Trans., 10.
—— amalgam, 275.

Potassium and thallium chlorates, solubility of mixed crystals of, 266.
—— bismuth chloride, 788.
—— bismuthate, 414.
—— bromide, action of sulphuric acid on, TRANS., 95, 101.
—— calcium thiosulphate, 12.
—— chlorate and iodine, interaction of, TRANS., 925.
—— chromosulphate, 784.
—— citrates, 149.
—— ferricyanide, estimation of, 526.
—— —— use of, in gasometry, 536.
—— —— volumetric analyses by means of, 1527.
—— ferrocyanide and ferricyanide, use of, in analysis, 1129.
—— —— volumetric analyses by means of, 1527.
—— fluoroxyhypovanadate, 787.
—— fluoroxyvanadate, 786.
—— hydrogen tartrate, use of, for titrating standard acids and alkalis, 525.
—— imidosulphonate, TRANS., 952.
—— iodide, estimation of iodates in, 657.
—— lead iodides and bromide, 780.
—— manganese chloride, 781.
—— manganites, hydrated, 569.
—— nitrosoplati-iodide, 281.
—— palladiochloronitrite, 1284.
—— permanganate solution, stability of, 1524.
—— phosphotungstates, 1160.
—— platibromonitrite, 1284.
—— platichloronitrite, 1284.
—— platidichloronitrite, 1284.
—— platinoselenostannate, 281.
—— platinothiocyanate, 286.
—— platinum thiostannate, reduction of, 944.
—— platipentachloronitrite, 1284.
—— platipentiodonitrite, 1284.
—— platitetrabromonitrite, 1284.
—— platitetriodonitrite, 281, 1284.
—— platitribromonitrite, 1284.
—— platitrichloronitrite, 1284.
—— platobromonitrite, 281, 1284.
—— platochloronitrite, 1283.
—— platodibromonitrite, 1284.
—— platodichloronitrite, 1284.
—— platodi-iodonitrite, 1284.
—— sodium hydrogen imidosulphonate nitrate, TRANS., 964.
—— spectroscopic detection and estimation of, 913.
—— stannochlorides, 785.
—— strontium thiosulphate, 13.
—— thioplatinosate, 944.
—— tricarballylates and their heats of formation, 762.
Potassium-nepheline, artificial formation of, 1286.
Potatoes, cooked, composition of, TRANS., 227.
Potential contact, differences of, 553.
—— differences of, at the surfaces of contact of very dilute solutions, 671.
Præsodymium, emission spectrum of, 2.
Precipitates, apparatus for washing, 1513.
Prehnitene, bromo-, action of sulphuric acid on, 968.
—— mono- and dichloro-, 967.
Pressure and specific volume of saturated vapours, 263.
—— influence of, on the expansion of water by heat, 1382.
—— of saturated water vapour, 396.
—— unequal, equilibrium of chemical systems under, 1148.
Propaldehyde, action of zinc and ethyl chloracetate on, 1300.
—— condensation of, with aniline, 1191.
—— dibrom-, 809.
Propaldehydeaniline, 1191.
Propane, 1 : 3-dinitro-, 1061, 1415.
—— nitrotribromo-, 1064.
—— sodiodinitro-, 1061.
—— tetrabromodinitro-, 1062.
Propaneparadisazoanisoïl, dinitro-, 1062.
Propanedisazobenzene, dinitro-, 1062.
Propanedisazotoluene, dinitro-, 1062.
Propargylamine, derivatives of, 30.
Propargyldithiocarbamic acid, 30.
Propargylic acid diiodide, 431.
Propargylphenylcarbamide, 31.
Propenyldimethylapionol, 1315.
Propenylparadibromobenzoic acid, para-, 605.
Propenylparahomosalicenylazoxime-ω-carboxylic acid, 319.
Propiomesitylene, action of hydroxylamine hydrochloride on, 314.
Propionamide, α-diiodo-, 452.
Propionamidine nitrate, 951.
—— nitrite, 53.
Propionates, metallic, 140.
Propionic acid, α-amido-, 1336.
—— —— β-iodo-, action of, on ethyl thiocarbamate, 440.
—— acids, β-oximido-, configuration of, 1069.
Propionohydroxamic acid, 699.
Propionyldiorthotolylhydrazine, 843.
Propionyldiparatolylhydrazine, 844.
Propionyldiphenylhydrazine, 843.
Propionylorthotolylhydrazine, 843.
Propionylparatolylhydrazine, 844.
Propionylpropionic acid and its dioximes, 351.
Propoxybenzamide, 595

Propoxybenzonitrile, 595.
Propyl alcohol, action of bromine on, 809.
—— —— vapour tension of, 397.
—— benzenesulphonate, 1220.
—— benzoate, γ-amido-, 213.
—— chlorides, chlorination of, 1414.
—— formate, magnetism of, 672.
—— hexyl ketone, 35.
—— phenyl ether, γ-chloro-, 717.
Propylacridine, 343.
Propylamidoacetic acid, 804.
Propylaminenitrobenzamide, γ-bromo-, 14.
Propylamines and their derivatives, 804.
Propylazobenzene, nitro-, 575.
Propylbenzamide, γ-bromo-, 212.
—— γ-chloro-, 213.
Propylbenzophenone, para-, 488.
—— —— oximes of, 489.
Propylcarbamide, 1421.
—— dibromo-, 30, 578.
Propylcinnamylamide, β-bromo-, 215.
—— γ-bromo-, 215.
Propyldithiobiuret, α-, 704.
Propylene bromide, action of, on the sodium derivatives of ethyl acetoacetate and ethyl benzoylacetate, Trans., 67.
—— dibromo-, 420.
—— nitro-, 575, 1062.
—— nitrobromo-, 1064.
—— sodionitro-, 1062.
Propyleneazobenzene, nitro-, 1063.
Propyleneazometabromobenzene, nitro-, 1064.
Propyleneazopseudocumene, nitro-, 1064.
Propylenecarbamide, bromo-, 578.
Propyleneglycol, diacetin of, 1163.
Propylenemetazobenzoic acid, nitro-, 1064.
Propyleneorthazotoluene, nitro-, 1063.
Propyleneparazoanisoïl, 1064.
Propyleneparazophenetoïl, nitro-, 1064.
Propyleneparazotoluene, nitro-, 1063.
Propyl-group, intramolecular change of the, 43.
Propylidenaniline, 1191.
Propylisoformanilide, 708.
Propylisosuccinimide, 701.
Propylmetanitrobenzamide, β-bromo-, 213.
Propyl-α-naphthylamine, 1338.
Propyl-β-naphthylamine, 1338.
Propyloxamic acid, 804.
Propylparisopropyltoluene, ortho-, 985.
Propylpentenethiocarbamide, symmetrical, 702.
Propylphenylacetamide, β-bromo-, 214.
—— γ-bromo-, 215.
Propylphthalimide, 157.
Propylsuccinimide, 701.
Propyltricarballylic acid, 42.
Propyltrimethylammonium salts, 949.
—— —— bromo-, 950.
Proteïd, new, from human blood serum, 224.
Proteïds, calorific values of, 4.
—— colour reactions of, 1036.
—— in green and etiolated leaves, 520.
—— of maize, 379, 746, 749.
—— of the oat kernel, 1120.
Protocotoïn, 62.
—— action of potash and methyl alcohol on, 873.
—— derivatives of, 63, 874.
Protoplasm, new albumin from, 86.
Prussic acid poisoning, antidote for, 1019.
Pseudocumene, fluoro-, 968.
Pseudocumylparatolylcarbamide, 979.
Pseudonicotine oxide, 1010.
Pseudopelletierine, 1110.
Pseudosolution, Trans., 148.
Pseudothiocyanogen, properties of, 292.
Pseudotropine, 1366.
Ptomaïnes of infectious diseases, 1258.
Puleone, an isomeride of camphor, 627.
Puleonoxime, 627.
Pump, Sprengel, automatic replacement of mercury in, 8.
Pupin, 1501.
Putrefaction of bile, 518.
—— of milk, 1116.
Pyrazole-derivatives, 731.
—— —— formation of, from the dichlorhydrins and tribromhydrin, 884.
Pyrazoles, platinum compounds derived from, 885.
Pyrazolone-derivatives, constitution of, 145.
—— —— synthesis of, 634.
Pyrazolones, nomenclature of, 1004.
Pyrethrosin, 349.
Pyridine, action of chloromethyl alcohol on, 504.
—— carbonyl bromoplatinite, 352.
—— chloriodide, 1356.
—— α-chloro-, 209.
—— chloroplatinite, 352.
—— constitution of, 210.
—— hydrogen diaminechromium thiocyanate, 1001.
—— platinothiocyanate, 287.
Pyridine-bases, action of, on sulphites, 1103.
—— —— of the β-series, 628.
Pyridinebetaïne, preparation of, 1433.
Pyridinecarboxylic acids from berberine, 1357.

Pyridine-derivatives, preparation of, from the lactone of triacetic acid, TRANS., 721.
Pyridine-like bases in petroleum, 1357.
Pyridone, α-, 208.
Pyridylacrylic acid, 77.
Pyridylbromopropionic acid hydrobromide, β-, 77.
Pyridyldibromopropionic acid, 77.
Pyridylethylene, 77.
Pyridyllactic acid, α-, 76.
Pyridyllactic acid, β-, 78.
Pyridyl-ω-trichloro-α-hydroxypropane, 75.
Pyridyl-α-trichloropropylene, 76.
Pyrites, burnt, utilisation of, in the preparation of iron salts, 1281.
Pyrocinchonic anhydride, preparation of, 814.
Pyrogallaurin, 1470.
Pyrogallol, constitution of, 1446.
—— conversion of gallic acid into, 1314.
—— derivatives of, 715.
—— sodium derivatives of, 1313.
—— thermochemistry of, 764.
Pyromucamide, thio-, 831.
Pyrophenite from Harstigen mine, Sweden, 1412.
Pyrotartaric acid, normal, thermochemistry of, 1141.
Pyroxene, analyses of, 1409.
Pyroxene-family, 1408.
Pyroxenic rock, azure blue, from New Mexico, 1057.
Pyrrodiazole, 637.
Pyrrodiazolecarboxylic acid, 636.
Pyrrolidine, synthesis of, 131.
Pyrroline, determination of the constitution of homologues of, 74.
Pyruvic acid, condensation of, with dicarboxylic acids, 814.
—— —— dibromo-, action of hydroxylamine on, 815.
—— —— hydrazones, TRANS., 786.
—— —— magnetic rotation of, TRANS., 807, 836.
—— —— thiophenylhydrazine, 1326.
—— anilide and its hydrazone, 1440.
—— —— imidochloride, 1440.
—— orthotoluidide, 1441.

Q.

Quartz, 1055.
Quercitol, thermochemistry of, 764.
Quinaldine, β-chloro-, synthesis of, 505.
—— synthesis of, 1245.
Quinamyline, 1253.
Quinazolines, 217.
—— thio-, new synthesis of, 1495.
Quince-juice, a sugar from, 128.
Quinidine benzyl salts, 1250.
—— compounds of, with hydriodic acid, 83, 640.
—— diethiodide, 1250.
—— diethyl salts, 1250.
—— dimethiodide, 1250.
—— ethiodide, 1249.
—— ethobromide, 1249.
—— hydriodo- and its salts, 1364.
—— methiodide, 1249.
Quinindole-α-carboxylic acid, ana-, TRANS., 787.
Quinine, action of hydriodic acid on, 81, 83, 640.
—— behaviour of, with methyl iodide, 221, 892.
—— compounds of, with hydriodic acid, 83, 640.
—— conversion of cupreïne into, 1010.
—— detection of, in urine, 665.
—— dibromide, 1012.
—— dimethiodide, 1363.
—— homologues of, 1253.
—— hydrochlorides, 514.
—— hydrogen diaminechromium thiocyanate, 1001.
—— methiodides, 1363.
—— preparation of homologues of, 222.
—— salts, appearance of fluorescence in, TRANS., 789.
Quininesulphonic acid, 515.
Quinisopropyline, 1253.
Quinitol, 833.
Quinol, chlorotribromo-, TRANS., 592.
—— compound of, with phenylhydrazine, 49.
—— diisoamyl ether, 1444.
—— metachlorobromo-, TRANS., 562.
—— metadibromo-, TRANS., 562.
—— metadichlorobromo-, TRANS., 567.
—— metadichlorodibromo-, TRANS., 579.
—— paradichlorobromo-, TRANS., 565.
—— sodium compounds of, 1184, 1185.
—— thermochemistry of, 764.
—— trichlorobromo-, TRANS., 593.
—— trinitro-, derivatives of, 314.
Quinoline alkyl iodides, action of alkalis on, 878.
—— γ-amido-, 725.
—— ana-amido-, TRANS., 785.
—— γ-bromo-, 630, 875.
—— chloriodide, 1357.
—— ethiodide, oxidation of, 730.
—— hydrogen diaminechromium thiocyanate, 1001.
—— methyl hydroxide, oxidation of, 729.
—— nitration of, TRANS., 782.
Quinoline-derivatives, appearance of colour in, TRANS., 789.

Quinoline-derivatives, synthesis of, by means of alkyl acetoacetates, 78.
Quinoline-group, attempted synthesis of a nitramine of, 725.
Quinolinehydrazine, ana-, TRANS., 784.
Quinolinehydrazines, 212.
Quinolinemethylium alkyl oxides, nitro-bromo-, 881.
—— hydroxide, bromo- and nitro-derivatives of, 880, 881.
Quinolinemethylpyrazolone, ana-, 788.
Quinoline-α-phenylsulphonic acids, 1003.
Quinolines, amido-, 1488.
—— hydrazines of, TRANS., 782.
Quinolinesemicarbazide, ana-, TRANS., 786.
Quinoline-series, ketones of the, 1488.
—— —— quaternary ammonium bases of, 1358.
Quinolmetachlorobromo-, chlorination of, TRANS., 578.
Quinone, action of ethyl acetoacetate on, 608.
—— and its derivatives, physiological action of, 1115.
—— chlorotribromo-, TRANS., 590.
—— halogen derivatives of, TRANS., 558, 589.
—— isomeric change in the halogen derivatives of, TRANS., 558.
—— metachlorobromo-, TRANS., 562.
—— metadibromo-, TRANS., 561.
—— metadichloro-, TRANS., 559.
—— —— bromination of, TRANS., 576, 580.
—— metadichlorobromo-, TRANS., 566.
—— metadichlorodibromo-, TRANS., 578.
—— paradichloro-, TRANS., 558.
—— —— bromination of, TRANS , 572.
—— paradichlorobromo-, TRANS., 563.
—— paradichlorodibromo-, TRANS., 572.
—— trichlorobromo-, TRANS., 592.
Quinonehæmatin, 1115.
Quinoneoxime acetate, 1457.
—— benzoate, 1457.
—— benzoxide, 1457.
—— ethers, 1456.
—— ethoxide, 1457.
—— methoxide, 1456.
Quinones, action of bleaching powder and of hypochlorous acid on, 720, 859, 970.
Quinonimides, formation of, from amidoazo-compounds, 1476.
Quinopropyline, 1253.
Quinoxazines, 887.
Quinoxazones, 887.

R.

Rabbits, hydrophobic, catechol in the urine of, 1115.
Racemic acid solutions, sp. gr. of, 964.
Radicles, substituted alcohol, directly united with carbon or with nitrogen, characteristic difference between, 106.
Radish, cooked, composition of, TRANS., 227.
—— quantity of starch in the tubercles of the, 92.
Raffinose, estimation of, in vegetable products, 249.
—— precipitation of, by ammoniacal lead acetate, 1294.
—— preparation of, from molasses, 422.
Rain as a source of nitrogen for vegetation, 233.
—— water, ammonia in, 381, 909.
Ramie plant, composition of, 1511.
Reaction, velocity of. See Velocity.
Realgar, analysis of, 657.
—— from the Yellowstone National Park, 283.
Rectorite, 22.
Refraction and dispersion of sodium chlorate, 1.
—— molecular, of nitrogen compounds, 933.
—— —— of solid chemical compounds in their solutions, 929.
—— —— of sulphines, 34.
Refractive index, density, molecular weight, and diathermanous power of a substance, relation between, 1.
—— indices and compressibility of liquids, relations between, 669.
—— —— of saline solutions, 929.
—— power of certain organic compounds at different temperatures, TRANS., 287.
—— powers of isocyanides and nitriles, 757.
Resazurin, formula of, 164.
Resin, detection of, in bees'-wax, 923.
—— of *Pinus abies*, terpenes from, 625.
—— oil, detection of, in terebenthene, 923.
Resins from *Pinus laricio* and *Picea vulgaris*, 204.
—— natural, 204.
—— of *Ficus rubiginosa* and *F. macrophylla*, TRANS., 916.
Resorcenylamidoxime, β-, 317.
Resorcinol diethyl ether, action of nitrous acid on, 44.
—— —— —— nitroso-, 45.
—— ethyl ether, nitroso-, 44.
—— heptachloro-, compounds derived from the so-called, 1186.
—— sodium compounds of, 1184, 1185.

Resorcinol, tetrachloro-, 1462.
—— thermochemistry of, 764.
Resorcinol-blue, Weselsky's, synthesis of, 163.
Resorcinoldisazobenzene, 977.
—— symmetrical, 977.
Resorcinyl orthacetate, 309.
Resorcylaldoxime, β-, 317.
Resorcyldialdoxime, 317.
Resorcylonitrile, β- 317.
Respiration, air vitiated by, 1502.
—— apparatus, 1257.
—— of plants under lessened oxygen tension and when injured, 1259.
Respiratory value of hæmocyanin, 1370.
Retiform tissue, 1113.
Retinite, 573.
Rhamnolactone, polarisation phenomena of, 1341.
Rhamnonic acid, polarisation phenomena of, 1431.
Rhamnose from frangulin, TRANS., 7.
—— multirotation of, 1420.
—— thermochemistry of, 763.
Rhamnus prushiana, cascarin from, 1483.
Rhodeochromium salts, 782.
Rhodinaldehyde, 203.
Rhodinol, 203, 625.
Rhodinolic acid, 203.
Rhodium-bases, constitution of, 783.
Rhodosochromium salts, 782.
Rhyolites, minerals in hollow spherulites of, 23.
Ribonic acid, 438.
Ribose and its derivatives, 439.
Rice, effect of excessive liming on the growth of, 94.
Ricinelaïdic acid, oxidation of, 1304.
Ricinoleïc acid, oxidation of, 1304.
Riebeckite from Michigan, 793.
Rings, closed, hydrogenation of, 1040.
—— —— nomenclature of, PROC., **1892**, 127.
Rock of the Jiwaara, in Finland, 1058.
Rocks, acid, reproduction of, 23.
Rock-salt from Torda and from Vizakna, 1054.
Rosaniline, formation of, 340.
Rose oil, German and Turkish, 203, 625.
Rosin, estimation of, in its mixtures with fatty acids, 389, 546.
—— oil, detection of, in fatty and mineral oils, 548.
Rotation, magnetic, of dissolved salts, PROC., **1892**, 12.
Rotatory power, laws of, and stereochemistry, 758, 759.
—— —— of diacetyltartaric-derivatives, 669.
Rubbadin, 1076.
—— action of nitric acid on, 1077.
Rubbadin, action of sulphuric acid on, 1077.
Rubidium antimony chlorides, 788.
—— bismuth chlorides, 789.
—— compounds, extraction of, from carnallite, 1395.
—— manganese chloride, 781.
Rubidium-carnallite, 1395.
Ruby from Burma, 1055.
Rumpfite, from Upper Styria, 417.
Ruthenium chloride, 688.
—— hydroxychloride, 688.
—— oxides, saline compounds of the lower with the higher, 282.
—— peroxide, action of light on, 282.

S.

Sabella, ash of the blood of, 1256.
Saccharin, specific rotatory power of, 1421.
—— thermochemistry of, 763.
Safrole, oxidation products of, 46, 310.
Salicylaldehyde, action of acetic chloride on chloro-, bromo-, and nitro-derivatives of, 1458.
—— ethylation of, 57.
—— reduction of, by zinc-dust and acetic acid, 168.
Salicyldiureïde, action of ethyl acetoacetate on, 56.
Salicylic acid, action of heat on, 1208.
—— —— compound of, with phenylhydrazone, 49.
—— —— condensation of nitrobenzaldehydes with, 621.
—— —— separation of, from benzoic acid, 1532.
Saline hydrates, formation of, at high temperatures, 119.
Salsify, cooked, composition of, TRANS., 227.
Salt, solution of a, in an indifferent salt solution and of a gas, analogies between, 397.
—— solutions, aqueous, viscosity of, 1044.
—— —— boiling, determination of the temperature of the steam arising from, TRANS., 495.
—— —— compressibility of, 766.
—— —— electrical behaviour of metals in, 393.
Salts, capillary constants of, at their melting points, 7.
—— changes of volume in solutions of, 706.
—— coloured, absorbent power of, and electrolytic dissociation, 757.
—— determination of the electrolytic

dissociation of, by means of solubility experiments, 1143.
Salts, dissolved, magnetic rotation of, Proc., **1892**, 12.
—— double, solubility of, 1145.
—— ethereal, normal isomeric, of the fatty series, calculation of the boiling points of, 260.
—— formation of layers in solutions of, in mixtures of water and organic liquids, 1146.
—— heat of dissolution of, in water, 676.
—— heat of formation of, in alcoholic solution, 262.
—— metallic, electromotive forces of, 255.
—— —— organic liquids as solvents for, 558.
—— mutual solubility of, in water, 8, 264.
—— solubility curves of pairs of, 1384.
—— state of, in solution, 397.
Samarium, spectra of, 780.
Samarskite from Colorado, 416.
Sand, siliceous, of Monte Soratte, 23.
Sandal wood, essence of, adulteration of, 1379.
Sandmeyer's reaction, use of sodium hypophosphite in, 305.
Santinic acid, 871.
Santonic acid, 1352.
—— —— oxidation of, 1353.
—— —— oxime of, 1352.
Santonin, derivatives of, 869.
Santoninamine, 869.
Santonine, detection and estimation of, 666.
Saponification by sodium ethoxide, 139.
Saponins, 350.
Sapotin, 724.
Sapotiretin, 725.
Sapotoxin from *Agrostemma githago*, 350.
Scarlet runners, cooked, composition of, Trans., 227.
Schiff's bases, 1189.
Scopolamine, 1255, 1366, 1498
Sea-kale, cooked, composition of, Trans., 227.
Sebacamide, 1180.
Sebacic acid, derivatives of, 1180.
Seeds, influence of vegetable poisons on the germination of, 228.
Selenium, allotropic states of, 405.
Semithiocarbazides, di-substituted, Trans., 1012.
Sepia officinalis, blood of, 648.
Serpentine rock from Borzanasca, 1058.
Serum and plasma, 1113.
—— human blood, new proteïd from, 224.
Serum, toxicity of 228.
Sesame oil, detection of, in olive oil, 1133.
Silicates, action of ammonium chloride at its dissociation temperature on, 772.
—— fractional analysis of, 945.
Silicic acid, colloïdal solutions of, Trans., 154.
—— —— estimation of, in fluorides, 1127, 1128.
Silicon carbide, 1050.
—— compounds, Trans., 453.
—— condition of, in cast iron, 19.
—— estimation of, in aluminium, 1130.
—— graphitoïdal, reducing action of, 115.
—— tetrachloride, action of, on substituted phenylamines, Trans., 453.
—— —— reactions of, 1273.
—— thiochloride, 404.
Silk, nitrated, 1111.
—— rotatory power of, 254, 645.
—— specific gravity of, 1036.
—— tissue, detection of vegetable fibre in, 667.
Silver, absorption of oxygen by, 943.
—— acetate, action of iodine on, 1301.
—— —— dry distillation of, 37.
—— acetylide, 1416; Proc., **1892**, 109.
—— action of chlorine and of bromine on, 118.
—— action of nitric acid on, 1403.
—— allotropic, 15, 116, 405.
—— and lead, separation of, 1522.
—— barium phosphotungstate, 1160.
—— blue, 15.
—— caproate, action of iodine on, 1301.
—— chloride, action of light on, 775; Trans., 728.
—— —— solution of, in aqueous ammonia, 1154.
—— colloïdal, 117, 941.
—— —— pure, preparation of, 775.
—— electrolytic detection of, 541.
—— electrolytic separation of, from osmium, 920.
—— estimation of, by means of hydroxylamine hydrochloride, 662.
—— estimation of small quantities of, in base metals, 1525.
—— hydrosulphide, Trans., 132.
—— imidosulphonates, Trans., 974.
—— lowering of the freezing point of bismuth by, Trans., 895.
—— lowering of the freezing point of cadmium by, Trans., 900.
—— lowering of the freezing point of lead by, Trans., 907.

Silver nitride, 112.
—— nitrosilicate, 684.
—— ore, new, 1404.
—— organosol of, 775.
—— permanganate, decomposition of, 942.
—— permolybdate, 1160.
—— phenylacetylide, 831.
—— salts, compounds of thiourea with, Trans., 249.
—— —— of fatty acids, dry distillation of, 38, 293, 811.
—— —— organic, dry distillation of, 293.
—— slags, estimation of bismuth in, 919.
—— sulphite, 684.
—— zinc, and lead, separation of, in galena and blende, 1378.
Silver-cadmium alloy, analysis of, Trans., 913.
Sinapanpropionic acid, 441.
Siphon for hot liquids or for those evolving gases or vapours, 270.
Slag, estimation of, in wrought iron, Trans., 551.
Slags, estimation of phosphoric acid in, 382.
—— silver, estimation of bismuth in, 919.
Soap analysis, 550.
—— estimation of combined alkali in, 384.
Sodammonium, action of, on metals, 275, 773.
Sodium, action of, on chromic fluoride, 19.
—— alloys of, 773.
—— amalgam, 275.
—— ammonium imidosulphonate, Trans., 961.
—— and tin, alloy of, 572.
—— as a plant food, 1508.
—— bromide, action of sulphuric acid on, Trans., 101, 102.
—— carbonate and sodium hydrogen carbonate, solubility of, in solutions of sodium chloride, 116.
—— chlorate, refraction and dispersion of, 1.
—— chloride, cryoscopy of dilute solutions of, 1045.
—— —— in plants, 651.
—— —— influence of, on nitrogenous excretion, 904.
—— —— measurement of the vapour pressures of solutions of, Trans., 773.
—— citrates, 149.
—— ethoxide, saponification by, 139.
—— ethylthiosulphate, preparation and properties of, 799.
Sodium ferrinitrosonaphtholsulphonate, 346.
—— ferrite, hydrated, dehydrating action of glycerol on, 119.
—— fluoroxyvanadate, 786.
—— hydrogen sulphide, action of iodine on, 681.
—— hypophosphite, use of, in Sandmeyer's reaction, 305.
—— imidosulphonates, Trans., 954.
—— isopropoxide, 691.
—— —— thermochemistry of, 674.
—— lowering of the freezing point of bismuth when alloyed with, Trans., 892.
—— lowering of the freezing point of cadmium by, Trans., 897.
—— lowering of the freezing point of lead by, Trans., 904.
—— nitride, 112.
—— nitrite, analysis of, 1029.
—— permolybdate, 1160.
—— platinoselenostannate, 282.
—— separation of, from mercury and phosphoric and arsenic acids, 530.
—— stannibromide, 121.
—— sulphate, action of carbon on, in presence of silica, 565.
—— —— boiling point of a solution of, Proc., 1892, 94.
—— —— solubility of, 398.
—— thiosulphate, change proceeding in an acidified solution of, where the products of change are retained in the system, Trans., 176.
Soil, absorption of oxyhydrogen gas by, 377.
—— arable, kaolin in, 1026.
—— estimation of phosphoric acid in, 750.
—— influence of, on the assimilation of free nitrogen by plants, 372.
—— influence of the nature of, on vegetation, 1121.
—— inoculation, experiments on, 1512.
—— loss of nitrogen in the decomposition of nitrogenous matters in the, 374.
—— phosphoric acid in, 233, 750.
—— presence of boric acid in the products of, 93.
—— vegetable, estimation of sulphur in, and the forms in which it is present, 656.
—— —— spontaneous oxidation of, 655.
—— the phosphoric acid of, 233, 750.
Soils, action of lime on, 94.
—— arable, estimation of kaolin in, 1031.
—— —— fixation of atmospheric nitrogen by, 522.

Soils, fallow, influence of clay and organic nitrogen in, on the absorption of atmospheric nitrogen, the retention of nitrogen, and nitrification, 656.
—— inorganic substances in, 1513.
Solanaceæ, alkaloïds of, 231.
Solanum nigrum, alkaloïds of, 232.
—— *tuberosum*, alkaloïds of, 232.
Solubility curve, theory of the, 559.
—— curves of pairs of salts, 1384.
—— mutual, of salts in water, 8, 264.
—— of double compounds, 1047, 1385.
—— of double salts, 1145.
—— of gases in water, 107, 271.
—— of mixed crystals, 265, 560.
Solution, alteration of the conductivity of, by addition of a non-electrolyte, 1382.
—— and pseudo-solution, Trans., 148.
—— and suspension, connection between, Trans., 151, 165.
—— law of thermodynamical coincidence and its application to the theory of, 557.
—— nature of, 108.
—— passage of substances in, through mineral filters and capillary tubes, 1267.
—— state of salts in, 397.
—— the new theories of, 264.
—— theory of residual chemical affinity as an explanation of the physical nature of, 559.
Solutions, a new property of certain, Trans., 160.
—— application of thermodynamics to, 395.
—— aqueous, action at a distance of water vapour on, 936.
—— —— diffusion in, 1265.
—— —— salt, viscosity of, 1044.
—— —— specific gravities of, 765.
—— cane-sugar, cryoscopy of, 109, 678, 1046.
—— chemical equilibrium in, 1146.
—— colloïdal, nature of, 766.
—— —— pedetic motion in relation to, Proc., 1892, 17.
—— dilute, applications of gaseous laws to, 935.
—— —— cryoscopic behaviour of, 8, 678, 1045.
—— —— existence of acid or basic salts of monobasic acids in, 110.
—— —— of cane sugar, freezing points of, 678, 1046.
—— isohydric and non-isohydric, of acids, velocity of reaction in mixtures of, 936.
—— measurement of the osmotic pressure of, 556.
Solutions, measurement of the vapour pressures of, Trans., 769.
—— molecular refraction of, 929.
—— of a gas and of a salt in an indifferent salt solution, analogies between, 397.
—— of salts, changes of volume in, 766.
—— —— in mixtures of water and organic liquids, formation of layers in, 1146.
—— of some metallic chlorides, physical properties of, Trans., 339.
—— partially miscible, 1046.
—— saline, compressibility of, 766.
—— —— refractive indices of, 929.
—— —— temperature of steam arising from, Trans., 495.
—— saturated, 1047.
—— stochiometry of, 1382.
—— strong, and the dissociation hypothesis, 108.
—— sugar, sp. gr. of, 935.
—— theory of, 1045.
—— very dilute, determination of the freezing points of, 935.
—— —— —— potential differences at the surface of contact of, 671.
Solvents, behaviour of optically active substances in mixtures of two, 1137.
Sorbinose, thermochemistry of, 763.
Sorbitol, compounds of, with molybdic acid, 422.
—— occurrence of, in the fruit of the cherry laurel, 908.
Sparteïne, 1362.
Specific gravities of aqueous solutions, 765.
—— gravity of gases, determination of, 1267.
—— —— of sugar solutions, 935.
—— —— relation of E.M.F. to, 257.
Specific heat of aluminium, 673.
—— —— of liquids at temperatures above the boiling point, 761.
—— —— of the diamond, 761.
—— heats of liquids, calculation of, 2.
Specific inductive capacity, relation of, to latent heat of evaporation, 258.
Specific rotatory power of galactonic acid and galactonolactone, 1432.
—— —— —— of gluconic acid and gluconolactone, 1432.
—— —— —— of invert sugar and of dextrose obtained from cane sugar by means of invertase, Trans., 408.
—— —— —— of rhamnonic acid and rhamnolactone, 1431.
—— —— —— of rhamnose and the saccharins, 1420.
—— —— —— of tartaric acid and its salts, 1308.
—— —— —— of xylose, 1420.

Specific volume and pressure of saturated vapours, 263.
Spectra, absorption, of thin metallic films, 1037.
—— emission, of neodymium and præsodymium oxides and of luminous solids containing neodymium, 2.
—— of samarium, 780.
Spectroscopic detection and estimation of potassium, 913.
Spectrum, absorption, of hæmatin, sensitiveness of, 1369.
—— of gallium, 930.
—— of hydrogen, Hasselberg's second or compound, 1381.
Spermine, supposed reaction of, 1300.
Spessartine from Virginia, 1411.
Spinach, cooked, composition of, TRANS., 227.
Spirits, analysis of, 387.
—— estimation of fusel oil in, 543.
—— examination of, for secondary constituents, 244.
—— of wine, detection of higher alcohols in, 1379.
Spring, hot mineral, at Finca Huracato, Salta, Argentine Republic, 574.
Stannibromides, 121.
Stannic acid, α-ortho-, 412.
Starch, colloïdal solutions of, TRANS., 156.
—— combination of iodine with, 801.
—— conversion of, into amyl alcohol by a bacterium, 90.
—— digestion of, by dogs, 516.
—— fixation of iodine by, 578.
—— in the fungus *Boletus pachypus*, 230.
—— iodide of, 578, 801, 1171.
—— product of the oxidation of, 1171.
—— quantity of, in the tubercles of the radish, 92.
—— thermochemistry of, 764.
Steam arising from boiling salt solutions, temperature of, TRANS., 495.
Stearic acid, action of bromine on, 695.
Stearolic acid, diiodo-, 470.
—— phenylhydrazide, 1428.
Steel, direct estimation of aluminium in, 102.
—— estimation of carbon in, 913.
—— estimation of chromium in, 538.
—— estimation of manganese in, 916, 1030.
—— estimation of nitrogen in, 237.
—— estimation of phosphorus in, 528, 529, 911.
—— estimation of sulphur in, 382.
—— estimation of tungsten in, 539.
Stereochemical models of organic molecules, 679.
Stereochemistry and the laws of rotatory power, 758, 759.
—— and the oximes, 50.
—— of diacetyltartaric acid, 758, 759.
Stilbene, formation of, from the polymeric thiobenzaldehyde, 184.
—— paradinitrorthodichloro-, 444.
—— substitution products of, 718.
Stilbene-series, isomeric change in, 1224.
Stomach, estimation of free hydrochloric acid in the, 236, 1125.
Stomach-contents, estimation of peptones in, 1136.
Straw, aërobic nitrate-reducing ferment in, 1259.
Stromeyerite from California, 1407.
Strontium and calcium, separation of, 915.
—— —— separation of, as chromates, 914.
—— barium, and calcium, separation of, 660.
—— carbonate, action of potassium sulphate on, 1276.
—— chloride, solubility of, 398.
—— chromate, solubility of, in dilute alcohol, 914.
—— nitride, 566, 776.
—— phosphates, 1156.
—— potassium thiosulphate, 13.
—— salts, physiological action of, 227.
—— —— pure, preparation of, 1277.
—— —— removal of barium from, 776.
—— tartrate, behaviour of, with plastered wines, 93.
—— volumetric estimation of, 1521.
Strychnine, 1012.
—— hydrogen diaminechromium thiocyanate, 1001.
Suberic acid, thermochemistry of, 1041.
Substitution in the fatty series, 577, 1414.
Succinamide, asymmetrical diiodo-, 453.
Succinendiamidoxime, formation of, 137.
Succinic acid, action of hydroxylamine on derivatives of, 136.
—— —— amido- and anilido-derivatives of, 819.
—— —— separation of malic acid from, 1531.
—— —— thermochemistry of, 1041.
—— diamide, imido-, 820.
Succinimidine nitrite, 53.
Succinimidoxime, 136.
Succinylphenylhydrazide, β-, 1494.
Succus entericus, human, 1368.
Sugar, analysis of, 388.
—— cane-, freezing points of dilute solutions of, 678, 1046.

Sugar, cane-, invert sugar and dextrose or levulose, examination of mixtures of, 248.
—— —— solutions, cryoscopy of, 109, 678, 1046.
—— —— sp. rot. power of, in dilute solution, 801.
—— —— thermochemistry of, 764.
—— disappearance of, from the blood, 363.
—— formation of, from peptones in blood, 1502.
—— formation of, in the organism, 1113.
—— formation of, in the organism when oxygen is deficient, 362.
—— from linseed, 1293.
—— from quince juice, 128.
—— in blood, 743.
—— invert, specific rotatory power and cupric reducing power of, Trans., 408.
—— milk-, behaviour of, in a diabetic 903.
—— —— thermochemistry of, 764.
—— potato-starch-, recognition of, in wine, 922.
—— products, estimation of calcium salts in, 1377.
—— solutions, sp. gr. of, 935.
Sugar-cane, healthy and diseased, analyses of, 1372.
Sugars, aromatic, 1447.
—— change of, in the alimentary canal, 902.
—— disappearance of the multirotation of, in ammoniacal solution, 1419.
—— distribution of, in *Boletus edulis* and *B. aurantiacus*, 519.
—— estimation of, by means of Ost's copper solution, 387.
—— richer in carbon from glucose, 1164.
—— thermochemistry of, 933.
Sulphanilic acid, transformation of, into sulphanilocarbamic acid in the animal economy, 903.
Sulphanilocarbamic acid, 904.
Sulphatammon, Trans., 949.
Sulphates, anhydrous, crystallised, 941.
—— from California, 1407.
—— metallic, efflorescence of, 1271.
—— volumetric estimation of, 1377.
Sulphide solutions, physical constitution of, Trans., 137.
Sulphides, inorganic, estimation of sulphur in, 657.
—— metallic, action of ferric chloride on, 18, 278.
—— soluble, volumetric estimation of, 1515.
Sulphines, molecular refraction and dissociation of solutions of, 34.
Sulphinic acids, tautomerism of, 623.
Sulphinic-derivatives and their analogies to compounds of organic amines, 34.
Sulphite and thiosulphate, action of iodine on a mixture of, Trans., 1083.
Sulphobenzaldehyde, bromo- and hydroxy-derivatives of, 337.
Sulphobenzamidinic acid, 714.
Sulphobenzoic acid, meta-, orthamido-, 333.
—— —— —— orthobromo-, 333.
—— —— —— paramido-, 332.
Sulphobenzoic acid, ortho-, nitro-, 479.
Sulphobutyric acid, β-, 424.
Sulphonal, physiological action of, 1507.
Sulphones, chemical and physiological relations of, 153.
Sulphonic acid, alkyl salts of, 1219.
—— acids, anhydrides of, Proc., **1892**, 41.
—— —— preparation of ethereal salts of, Proc., **1891**, 184.
—— chlorides, action of alcohol on, Proc., **1891**, 184.
Sulphur, action of, on metallic solutions, 770.
—— action of, on the alkaline earths, 770.
—— action of, on the alkalis, 770.
—— action of, on water at 100°, 770.
—— and phosphorus, compounds of, 14.
—— allotropic states of, 405.
—— combustion of, in oxygen, 679.
—— estimation of, 382, 1375.
—— estimation of, in galena, 658.
—— estimation of, in inorganic sulphides, 657.
—— estimation of, in organic substances, 382.
—— estimation of, in red copper, 753.
—— estimation of, in vegetable soil, 656.
—— flowers of, action of sulphurous acid on, Trans., 199.
—— forms in which present in vegetable soils, 656.
—— from the Yellowstone National Park, 283.
—— in iron, estimation of, 1376.
—— in steel and iron, estimation of, 382.
—— insoluble, 1389.
—— plastic, formation of, from sulphur vapour, 1150.
—— tetroxide, 111.
Sulphuric acid, amides and imides of, 1389.
—— —— and water, contraction on mixing, 271.
—— —— combined, estimation of, 104, 538.

Sulphuric acid, combined, volumetric estimation of, 1515.
—— —— cryoscopic behaviour of weak solutions of, 678.
—— —— dilute, density and composition of, 271.
—— —— estimation of, 659.
—— —— formation of, in burning coal-gas, 1151, 1374, 1389.
—— —— in urine, volumetric estimation of, 1377.
—— —— solutions, densities of, 271, 272.
Sulphurous acid, action of, on flowers of sulphur, TRANS., 199.
—— —— complex salts of, 564.
—— —— constitution of, 1324.
—— anhydride, decomposition of, by carbon at high temperatures, 681.
—— —— microscopic detection of, 237.
Sulphuryl holoxide, 401.
Superphosphates, analysis of, 1125.
Supersaturation, 398.
Suspension and solution, connection between, TRANS., 151, 165.
Syrup, estimation of calcium salts in, 1377.

T.

Tænite from the Welland meteoric iron, 24.
Talomucic acid, 299.
Talonic acid, 299.
Talose, 299.
Tannic acid, physiological action of, 905.
Tannin analysis, Lowenthal's method of, 667.
—— derivatives of, 181.
—— estimation of, 1135.
—— estimation of, in barks, 390.
—— from chestnut wood, 716.
Tariric acid, 582.
Tartar, estimation of, in sweet wines, 1531.
Tartaric acid and its salts, specific rotatory power of, 1308.
—— —— detection of, in citric acid, 546.
—— —— separation of malic acid from, 1531.
—— —— solutions, sp. gr. of, 964.
—— —— synthesis of, 822.
—— diphenylhydrazide, action of carbonyl chloride on, 511.
Tartarotartaric acid, 965.
Tartranilide, acetyl derivatives of, 54.
—— preparation of, 54.
Tartrates, dissociation in dilute solutions of, 588, 1144.
Tartromalic acid, 589.
Tartronic acid, alkali salts of, 675.
—— —— thermochemistry of, 675.
Tea, analysis of, 926.
Teak, mineral substances in, 230.
Teas, preparation of, 1371.
Teeth, influence of various salts on the composition of, 647.
Tellurium from Faczebaya, 1054.
Temperature and solubility, law of the connection between, 559.
—— change of the empirical and theoretical isothermals of mixtures of two substances with the, 259.
—— influence of, on the refractive power of certain organic compounds, TRANS., 287.
—— volume and E.M.F., changes of, on mixing electrolytes, 930.
Temperatures, critical, of mixed liquids, 262.
—— high, optical measurement of, 761.
—— of saturated vapours of various liquids under the same pressure, 1143.
—— very low, physical and chemical phenomena at, 1138.
Tension, maximum, with which hydrogen is set free from solutions by metals, 561.
Teraconic acid, synthesis of, 427.
Terbium earth, 1400.
Terebenthene, 624, 625.
—— detection of resin oil in, 923.
Terecamphene, 624, 635.
Terfâs, relation between truffles and, 654.
Terfezia bouderi, analysis of, 654.
—— *claveryi*, analysis of, 654.
—— *hafazi*, analysis of, 654.
Terpene, dextro-, from Russian turpentine, degree of saturation of, 1350.
Terpenes and their derivatives, 200, 347, 623, 625, 722, 1100.
—— from the resin of *Pinus abies*, 625.
Terpin hydrate, action of hydriodic acid on, 867.
—— —— from eucalyptus oil, 1235.
Terpinol hydrate, reduction of, 1351.
Tetrabenzoyloxamide, 1084.
Tetrabenzylcarbamide, 1083.
Tetrabenzyltrimethylenetrisulphone, 592.
Tetracetyleuxanthic acid, 1354.
Tetracetylhydrindigotin, 480.
Tetracetylpenterythritol, 128.
Tetradecylacetylene, 1163.
Tetradymite from Zsupkó and from Rézbánya, 1054.

Tetrahydrobenzylidene-2 : 6-lutidine, 1361.
Tetrahydroketoquinoxalines, 886.
Tetrahydro-2-methylpyridine, Δ^2, 1243.
Tetrahydro-α-naphthoic acid, 192.
Tetrahydro-β-naphthoic acid, 194.
Tetrahydronaphthylanisoïl, 1445.
Tetrahydronaphthylphenol, 1445.
Tetrahydrophthalic acid, cisΔ^4-, 1216.
Tetrahydropicoline, Δ^2-, 1243.
Tetrahydropinene, 998.
Tetrahydropyrazine, 633.
Tetrahydropyridine, 1484.
Tetrahydropyridine-derivatives, synthesis of, and conversion of, into piperidine derivatives, 1243.
Tetrahydroquinoline, dinitro-, 726.
—— oxidation of, 1104.
Tetrahydroquinoline-derivatives, oxidation of, 355.
Tetrahydroquinolylcarbamide, 725.
—— dinitro-, 726.
Tetrahydrothioquinazoline, 1496.
Tetrahydroxyaurindicarboxylic acid, 1469.
Tetrahydroxybenzophenone and its derivatives, 1225.
Tetraketohexamethylene hydrate, trichloro-, 835.
—— tetrachloro-, 836.
—— tribromo, 836.
Tetralkylammonium iodides, formation of, 133.
Tetramethylbenzamidobenzophenone, action of nitrous acid on, 185.
Tetramethylbenzidine, metadiamido-, 1222.
Tetramethyldiamidoarsenobenzene, 1321.
Tetramethyldiamidobenzhydrol, condensation of, with xylidine, mesidine, pseudocumidine, isoduridine, and prehnidine, 188.
Tetramethyldiamidodiphenylmethoxymethylquinolylmethane, 190.
Tetramethyldiamidophenylquinolylmethane, 190.
Tetramethylene, derivatives of, Trans., 36.
—— diethyl glycol, Trans., 58.
—— ethyl ketone, Trans., 51.
—— —— —— sodium hydrogen sulphite compound of, Trans., 53.
—— —— ketoxime, Trans., 54.
—— methyl ketone, Trans., 47.
—— —— ketoxime, Trans., 49.
—— phenyl ketone, Trans., 59.
—— —— ketoxime, Trans., 61.
Tetramethylenecarboxylic acid, bromo-, Trans., 41.
—— —— dissociation constant of, Trans., 705.
Tetramethylenecarboxylic acid, preparation of, Trans., 40.
—— acids, melting points of, 1040.
—— chloride, preparation of, Trans., 41.
Tetramethylenedicarboxylic acid, α-, dissociation constant of, Trans., 705.
—— acids, 1306.
—— —— thermochemistry of, 1041.
Tetramethylene-ethylcarbinol, Trans., 54.
Tetramethylene-ethylcarbinyl acetate, Trans., 56.
Tetramethylenemethylcarbinol, Trans., 50.
Tetramethylenephenylcarbinol, Trans., 62.
—— polymeride of, Trans., 65.
Tetramethylenepropyl bromide, Trans., 58.
—— iodide, Trans., 57.
Tetramethylorthophenylenediamine, 1474.
Tetramethyltriamidodiphenylmethoxytolylmethane, 190.
Tetramethyltriamidodiphenyltolylmethanes and their derivatives, 187.
Tetra-β-naphthylcarbamide, dithio-, 166.
Tetraphenylcarbamide, dithio-, 165.
—— thio-, 165.
—— tetraphenylthiodithiosemicarbazide, 1326.
Tetraphenylthiophen, 185.
Tetratolylcarbamide, para-, 1083.
Tetratolyloxamide, para-, 1084.
Tetravinylpyridine, 1483.
Tetrazole, 1009.
Tetrazoleazodimethylaniline, 1299.
Tetrazoleazo-β-naphthylamine, 1299.
Tetrazotic acid, amido-, 1299.
Tetrethylacetone, 1188.
Tetrethyldiamidoarsenobenzene, 1321.
Tetrethyleuxanthic acid, 1354.
Tetrethyltriamidodiphenyltolylmethane, 189.
Tetrethyltrimethylenetrisulphone, 592.
Tetrole-nuclei, constitution of, 302.
Tetrolic acid, 961.
Tetrylenedicarboxylic acetoanhydride, 1307.
—— acetochloranhydride, 1307.
—— acid, symmetrical, 1306.
Thallium and potassium chlorates, solubility of mixed crystals of, 266.
—— chlorochromate, 568.
—— chromate, 567.
—— estimation of, 238.
—— hypophosphate, 403.
—— lowering of the freezing point of cadmium by, Trans., 903.
—— potassium chromate, 568.

Thallium sesquioxide, 568.
Thallium lead alloy, analyses of, TRANS., 914.
Thaumasite from Kjölland, 1407.
Thermal value of the hydroxyl groups in glycol, 576.
Thermochemistry of bibasic organic acids, 395, 1140.
—— of compounds of chlorine with iodine, 1387.
—— of dibromomalonic acid, 1140.
—— of di-, tri-, tetra-, penta-, and hexa-methylene rings, 1041.
—— of disodium glycol, 421.
—— of guanidine and nitroguanidine, 1142.
—— of hydrazine, 933, 1143.
—— of hydroxylamine, 1143.
—— of malic acid, 260.
—— of monosodium and disodium catechol, 1184. 1185.
—— of monosodium mannitol, 800.
—— of monosodium and disodium resorcinol and quinol, 1185.
—— of persulphuric acid and its salts, 931.
—— of phenol, 1041.
—— of sodium isopropoxide, 674.
—— of sodium pyrogalloi, 1313.
—— of sugars, 931.
—— of tartronic acid, 675.
—— of the carbohydrates and polybasic alcohols and phenols, 763.
—— of the cinnamic acids, 469.
—— of the hydroxybenzenes, 1446.
—— of the oxime of opianic anhydride, 459.
—— of the substitution of radicles in union with carbon and nitrogen respectively, 1141.
Thermodynamical coincidence, law of, and its application to the theory of solution, 557.
Thermodynamics, second law of, and its application to chemical phenomena, 3.
Thermoelectric phenomena at the contact of two electrolytes, 1037.
Thetincarboxylic acids, 1433.
Thiacetic anhydride, 300, 581.
Thiamides, action of ethylenediamine on, 1247.
Thiazole, 313.
—— compounds of, 215.
Thienylisoxazolic acid, 304.
Thienylphenylpyrazole, 304.
Thienylphenylpyrazolic acid, 303.
Thiobiurets, 703.
Thiocarbamates, reactions of, 1318.
Thiocarbamide, silver compounds of, 441; TRANS., 2 9.
Thiocarbamides, 702.
—— action of ethylene bromide on, 466.
Thiocarbamides, aliphatic, action of oxidising agents on, 292.
—— aromatic, action of thiocarbonyl chloride on, 983.
—— unsymmetrical, action of acetone and bromacetophenone on, 216.
Thiocarbaniltolyloxamethane, 599.
Thiocarbimides, compounds of, with aldehyde-ammonias, TRANS., 509.
Thiocarbonyl-β-dinaphthylthiocarbamide, 984.
Thiocarbonyldiparatolylthiocarbamide, 984.
Thiocarbonylthiocarbanilide, 983.
Thiocyanacetone, 1425, 1426.
—— estimation of, 1426.
Thiodiphenylcarbamic chloride, 164.
Thiohydantoic acid, action of phenylhydrazine on, 966.
Thiole, 312.
Thionessal, 185.
—— substitution products of, 718.
Thionyl chloride and aromatic hydrazones, 1324.
Thiophen mercuric chloride, 828.
—— nitrile, 831.
—— tetrabromo-, oxidation of, 302.
Thiophenaldoximes, 1435.
Thiophenantialdoxime, 1435.
Thiophenchloropnosphine and its derivatives, 966.
Thiophendicarboxylic acid, αβ-, 830.
—— —— bromo-, 831.
Thiophendiethylmethylphosphonium iodide, salts, 966.
Thiophendiethylphosphine, 966.
Thiophenoxychlorophosphine, 966.
Thiophenphosphinic acid, 966
Thiophenphosphinous acid, 966.
Thiosulphate and sulphite, action of iodine on a mixture of, TRANS., 1083.
—— solutions, preservation of, 1514.
Thiosulphates, 12, 1418.
Thiosulphonates, aromatic, 990.
Thiosulphonic acids, aromatic, 478.
Thiosulphuric acid, decomposition of, TRANS., 176.
Thiotolene mercuric chloride, β-, 829.
Thiourea, action of nitrous acid on, TRANS., 525.
—— and ammonium thiocyanate, compound of, 1309.
—— compound of silver bromide with, TRANS., 251.
—— compound of silver chloride with, TRANS., 252.
—— compound of silver cyanide with, TRANS., 253.
—— compound of silver iodide with, TRANS., 252.
—— compound of, with aldehyde-ammonia, TRANS., 510.

Thiourea, compound of, with isovaleraldehyde-ammonia, Trans., 513.
—— compounds of silver nitrate with, Trans., 250.
—— compounds of, with aldehyde-ammonias, Trans., 509.
—— properties of, 1309.
—— silver compounds of, Trans., 249.
Thioureas, Proc., **1892**, 96.
—— substituted, isomerism amongst the, Trans., 536.
Thorium and uranous sulphates, isomorphous, 571.
Thymol, 1078.
—— refractive power of, at different temperatures, Trans., 305.
Thymolglycuronic acid, 1116.
Tiglic acid, constitution of, 1304.
Tilias, oil from the seeds of, 92.
Tin, action of nitric acid on, 1402.
—— and sodium, alloy of, 572.
—— antimony, and arsenic, detection of, 918.
—— —— —— separation of, Trans., 424.
—— bismuth, cadmium, and lead, separation of, 754.
—— cadmium, and gold, estimation of, in alloys, 1030.
—— double halogen salts of, 785.
—— estimation of, 1129.
—— lowering of the freezing point of bismuth by, Trans., 896.
—— lowering of the freezing point of cadmium by, Trans., 901.
—— lowering of the freezing point of lead by, Trans., 908.
Tin. See also Stannic.
Tin-ores, analysis of, 540.
Tirmania africana, analysis of, 654.
Tissue, retiform, 1113.
Tissue-fibrinogens, 646.
Titanic oxide, distribution of, on the earth, 791.
Titaniferous iron ore from the Fichtelgebirge, 1406.
Titanium, decomposition of minerals containing, 664.
—— estimation of, in titanium-aluminium, 1131.
—— sesquioxide, action of nitric oxide on, 1152.
Tolallyl sulphide, 185.
Tolane sulphide, 185.
Tolenylamidine nitrite, para-, 53.
Tolidine, metamidortho-, 852.
—— metanitrortho-, 852.
—— polymethylene bases from, 1223.
Tolidinedisulphonamide, 1468.
Tolidinedisulphonic acid, ortho-, 1466.
Tolidinesulphonic acid, 1467.
Tolualanine, nitro-, 1359.
Toluamide, imidodiortho-, 712.
—— imidodipara-, 712.
Toluene, bromination of, Trans., 1025.
—— diamido-, action of formaldehyde on, 1496.
—— interaction of bromine and, Trans., 1023.
—— 1 : 2 : 5-dichloro-, sulphonation of, Trans., 1050.
—— 1 : 3 : 4-dichloro-, sulphonation of, Trans., 1060.
—— metachloro-, sulphonation of, Trans., 1075.
—— orthobromo-, bromination of, Trans., 1031.
—— orthochloro-, sulphonation of, Trans., 1072.
—— orthonitro-, action of chlorine on, in presence of sulphur, 1437.
—— parabromo-, bromination of, Trans., 1032.
—— parachloro-, sulphonation of, Trans., 1078.
—— paramidorthochloro-, 445.
—— refractive power of, at different temperatures, Trans., 297.
—— 1 : 3 : 4 : 5-trichloro-, Trans., 1070.
Tolueneazocyanocamphors, ortho- and para-, 1343.
Toluenediazoacetotoluidide, 459.
Toluenehydrazoparacresol, para-, 974.
Toluenemetasulphonic acid, orthometadibromo-, Trans., 1038.
Toluneparasulphonic acid, bromination of the potassium salts of, Trans., 1027.
Toluenes, ortho- and para-bromo-, preparation and properties of, Trans., 1026, 1027.
Toluenesulphonic acid, 1 : 2 : 5-dichloro-, derivatives of, Trans., 1051.
—— —— 1 : 3 : 4-dichloro-, derivatives of, Trans., 1061.
—— —— —— hydrolysis of, Trans., 1068.
—— —— metachloro-, Trans., 1075.
—— —— ortho-, 1 : 2 : 5-orthobromo-, Trans., 1041.
—— —— —— 1 : 2 : 5-orthochloro-, Trans., 1040.
—— —— orthochloro-, Trans., 1072.
—— acids, mono-, di-, and tri-chloro-, Trans., 1042.
—— —— ortho- and para-bromo-, Trans., 1023.
—— —— parachloro-, Trans., 1078.
Toluenethiosulphonic acid, reactions of, 478.
Toluic acid, meta-, parachloro-, 1201.
Toluic acid, ortho-, parabrom-, nitration and bromination of, 1207.
Toluic acid, para-, 5 : 2-amidochloro-para-, 172.

Toluic acid, para-, 6 : 3-amidochloro-, 173.
—— —— —— 2 : 3-azimido-, 177.
—— —— —— 5 : 2-bromochloro-, 173.
—— —— —— 2 : 3-diamido-, 176.
—— —— —— 2 : 5-diamido-, 176.
—— —— —— 3 : 5-diamido-, 177.
—— —— —— 2 : 3-dibromo-, 175.
—— —— —— 2 : 6 dibromo-, 175.
—— —— —— 3 : 5-dibromo-, 176.
—— —— —— 2 : 3-dinitro-, 176.
—— —— —— 2 : 5-dinitro-, 176.
—— —— —— 2 : 6-dinitro-, 177.
—— —— —— 3 : 5-dinitro-, 177.
—— —— —— metachloro-, nitration of, 173.
—— —— —— 2 : 5-nitramido-, 177.
—— —— —— 3 : 5-nitramido-, 178.
—— —— —— 2 : 5-nitrobromo-, 178.
—— —— —— 3 : 2-nitrobromo-, 175.
—— —— —— 3 : 5-nitrobromo-, 178.
—— —— —— 5 : 2-nitrobromo-, 174.
—— —— —— 6 : 2-nitrobromo-, 175.
—— —— —— 2 : 3-nitrochloro-, 174.
—— —— —— 3 : 2-nitrochloro-, 173.
—— —— —— 5 : 3-nitrochloro-, 174.
—— —— —— orthobromo-, nitration of, 175.
—— —— —— orthochloro-, nitration of, 172.
—— —— —— orthonitro-, nitration of, 176.
Toluic acid, 4 : 1 : 3-sulphamido-, 1092.
Toluic acids, dibromortho-, 1207, 1208.
—— —— nitrobromortho-, 1207.
—— sulphinide, 1092.
Toluidine, commercial, assay of, 925.
Toluidine, meta-, parachloro-, 1201.
Toluidine, ortho-, action of benzyl chloride on, 48.
—— —— and furfuraldehyde, condensation of, 1452.
—— —— chloro-, conversion of, into chlorotoluene, TRANS., 1047.
—— —— —— conversion of, into dichlorotoluene, TRANS., 1049.
—— —— hydrogen diaminechromium thiocyanate, 1000.
—— —— influence of nucleal methyl on the properties of, 1319.
Toluidine, para-, chloro-, conversion of, into chlorotoluene, TRANS., 1058.
—— —— 5 : 2-nitrobromo-, 174.
—— —— 2 : 5-nitrochloro-, 172.
—— —— 6 : 2-nitrochloro-, 172.
—— —— 6 : 3-nitrochloro-, 173.
Toluidineazo-α-naphthol, ethyl and methyl ethers of, 863.
Toluidinemetasulphonic acid, ortho-, metabrom-, TRANS., 1037.
Toluidines, ortho- and para-, action of benzyl chloride on, 313.
Toluidinesulphonic acid, ortho-, Nevile and Winther's, constitution of, TRANS., 1036.
Toluidobutyric acid, α-ortho-, 1338.
Toluidobutyric acid, α-para-, 1338.
Toluidocinnoline, para-, 1494.
Toluidoisobutyric acid, α-ortho-, 1339.
Toluidoisobutyric acid, α-para-, 1339.
Toluidoisobutyric acid, β-para-, 1339.
Toluidoisobutyric acids, 1339.
Toluidopropionic acid, α-para-, 1337.
Toluidopropionic acid, β-para-, 1343.
Toluonitrile, ortho-, dibrom-, 1208.
Toluonitrile, para-, 2 : 6-dibromo-, 175.
—— —— 3 : 5-dibromo-, 176.
—— —— 2 : 6-dinitro-, 177.
—— —— 6 : 2-nitrobromo-, 175.
—— —— 5 : 2-nitrochloro-, 172.
—— —— 6 : 3-nitrochloro-, 173.
Toluyl methyl ketone, parabromometa-, 338.
Toluyldithiocarbamic acids, salts of, 56.
Toluylenaldehydenitrodimethoxybenzenylorthocarboxylic acid, 1249.
Toluylenediamine, ortho-, derivatives of, 709.
Toluyleneoxamide, 1208.
Toluylenephthalamidone, 1248.
Toluylxylide, ortho-, 491.
Tolyl cyanate, nitro-, 833.
—— isocyanide, ortho-, 1441.
—— —— para-, 1442.
—— methyl ketone, parabromometa-, 1200.
—— —— —— parachlorometa-, 1201.
—— —— ketoxime, parabromometa-, 1201.
—— —— —— parachlorometa-, 1201.
—— orthotolylcarbamate, ortho-, 832.
Tolyl-β-alanine, para-, 1343.
Tolylazimidobenzene, amidopara-, 1322.
Tolylazoparatolylthiobiazolone, para-, 512.
Tolylazoparatolyl-ψ-thiobiazolone, para-, 512.
Tolylazorthotolyldithiobiazolone, ortho-, 513.
Tolylazorthotolylthiobiazolone, ortho-, 513.
Tolylbenzenemetacarboxylic acid, meta-, 851.
Tolylcarbamide, para-, and its derivatives, 460.
Tolyldibenzylcarbamide, para-, 1083.
Tolyldifurylnaphthodihydroquinoxaline, 1476.
Tolyldimethylthiohydantoïn, ortho-, 150.
Tolyldimethylthiohydantoïn, para-, 150.
Tolyl-β-dimethyl-μ-thiomethylimidazole, ν-ortho-, 153
Tolyl-β-dimethyl-μ-thiomethylimidazole, ν-para-, 153.

Tolyldiphenylethohydronaphthazonium hydroxide, 1474.
Tolyldiphenylnaphthodihydroquinoxaline, 1474.
Tolylenedioxamethane, 603.
Tolylenedioxamic acid, 604.
Tolylenedioxamide, 603.
Tolylenemalonamide, 600.
Tolyleneoxamide, 599.
Tolylfurfurylcarbamide, ortho-, 43.
Tolylfurfurylthiocarbamide, 43.
Tolylglycocine, ortho-, derivatives of, 1333.
Tolylglycocine, para-, 1335.
—— —— and its derivatives, 1335.
Tolylhydantoïn, γ-para-, 828.
Tolylhydrazine phosphenite, para-, 1325.
Tolylhydrazinecamphoric acid, para-, 1481.
Tolylhydrazone, thionylpara-, 1324.
Tolylhydrazoparatolylthiobiazolone, para-, 512.
Tolylhydrazotolyldithiobiazolone, para-, 512.
Tolylhydroxypyrimidinecarboxylic acid, para-, 1008.
Tolylimidocarbonyl chloride, 1441.
Tolylimidodiacetamide, ortho-, 1335.
Tolylimidodiacetic acid, para-, 1336.
—— ditoluidide, para-, 1336.
Tolylimidodiacetimide, ortho-, 1335.
Tolylimidazole, ν-para-, 1329.
Tolylimidazolyl methyl sulphide, 1329.
Tolylimidazolyl-μ-mercaptan, ν-para-, 1328.
Tolylisoquinoline, β-para-, 475.
—— —— α-chloro-, 474
Tolyl-β-methyl-α-methoxy-μ thiomethylimidazole, ν-ortho-, 152.
Tolyl-β-methyl α-methoxy-μ-thiomethylimidazole, ν-para-, 152.
Tolyl-α-methylphthalimide, para-, 608.
Tolylmethylthiohydantoïn, ortho-, 150.
Tolylnaphthylenediamine, 1476.
Tolylorthazodibenzylamine, para-, 316, 890.
Tolylorthonaphthylenediamine, para-, and its anhydro- and thio-derivatives, 1473.
Tolylorthotolylsemithiocarbazide, para-, Trans., 1016.
Tolyloxamethane, amido-, 599.
—— nitro-, 601.
Tolyloxamic acid, amido-, 599, 601, 1208.
—— —— urethano-, 599, 1208.
Tolyloxamide, amido-, 602.
—— nitro-, 601.
Tolyloxanilide, amido-, 602.
Tolylparatolylsemithiocarbazide, ortho-, Trans., 1015.
Tolylphenylacetonitrile, 1094.
Tolylphenylketoximes, ortho-, 490.
Tolylphenylsemithiocarbazide, para-, Trans., 1013.
Tolylphthalimide, ortho-, preparation of, 1204.
Tolyltetrahydroketoquinazoline, para-, 1496.
Tolyltetrahydrothioquinazoline, 1496.
Tolylthiocarbazinic orthotolylhydrazide, ortho-, 513.
Tolylthiocarbazinic paratolylhydrazide, para-, 511.
Tolylthiocarbimide-aldehyde-ammonia, ortho-, Trans., 520.
Tolylthiohydantoïn, ortho-, 150.
Tolylurethane, amido-, 600, 1203.
—— paramido-, 601.
—— paranitro-, 601.
Tomato, cooked, composition of, Trans., 227.
Tourmaline, formula of, 1410.
—— red, from Siberia, 573.
Toxic action of blood and various tissues, 228.
Toxic principles of *Amanita pantherina*, 232.
Toxicity of serum, 228.
Transpiration, 1267.
Transportation of solids in a vacuum by the vapours of metals, 1386.
Trees, occurrence of calcium oxalate in the bark of, 1370.
Trehalose, detection and extraction of, 545.
—— thermochemistry of, 764.
Triacetic acid, lactone of, preparation of pyridine derivatives from, Trans., 721.
Triacetin, 289.
Triacetylglycerol, 289.
Triammonium imidosulphonate, anhydrous, Trans., 949.
—— —— hydrated, Trans., 948.
Triargentic imidosulphonate, Trans., 974.
Triazobenzene, physiological action of, 366.
Triazole, 735.
Triazolecarboxylic acid, 735.
Triazole-derivatives, 637.
Triazoles, nomenclature of, 889.
Tribenzyl orthothioacetate, 612.
Tribenzylcarbamide, 1083.
Tribenzylpyridine, 1365.
Tribenzylsulphonemethylmethane, 613.
Tribenzylsulphonephenylmethane, 613.
Tribromhydrin, symmetrical, formation of, 577.
Tricalcium phosphate, action of carbonic anhydride and of ferric hydroxide on, 408.
—— —— solubility of, in solutions of phosphoric acid, 684.

Tricarballylic acid, dissociation constant of, TRANS., 707.
Tricinnamtetra-ureïde, 57.
Tricyanides, formation of, from nitriles and acid chlorides, 1183.
Triethoxytriphenodioxazine, 158.
Triethyl orthothioacetate, 612.
Triethylamine platinothiocyanate, 286.
Triethylgallic acid, amido-, 716.
—— —— dibromo-, 715.
—— —— nitro-, 716.
Triethylidenecinchonine, 1252.
Triethylpyrogallol, amido-, 716.
—— nitro-, 716.
Triethylresorcinol, action of nitrous acid on, 44.
Triethylsulphonemethylmethane, 154.
Trifolium, analyses of, 522.
Trihydroxyaurindicarboxylic acid, 1469.
Trihydroxybenzophenone, bromo-, 1225.
—— derivatives of, 1224.
—— nitro-derivatives of, 1225.
—— sodio-, 1224.
Trihydroxyglutaric acid, second inactive, 437.
Trihydroxyquinoxaline, 734.
Trihydroxystearic acids prepared from ricinoleïc and ricinelaïdic acids, stereochemistry of, 1304.
Triketopentamethylene hydrate, dibromo-, 836.
—— tribromo-, 836.
—— trichloro-, 835.
Trimethylacetaldehyde, 39.
Trimethylacetic acid, solubility of salts of, 581.
Trimethylallylammonium iodide, 1295.
Trimethylamine, action of capryl iodide on, 806.
—— action of isoamyl iodide on, 805.
—— action of isobutyl iodide on, 805.
—— chloriodide, 1357.
—— ethylene bromide, 806.
—— —— iodide, 808.
—— hydrogen diaminechromium thiocyanate, 1000.
—— physiological action of, 366.
—— platinocyanate, 286.
—— pure, preparation of, 805.
Trimethylbenzaldehyde, 329.
Trimethylcarbinol, action of bromine on, 809.
—— sodio-, 1066.
Trimethylchlorethylammonium platinochloride, 807.
Trimethyldiamidobenzophenone, 185.
—— nitrosamine of, 185.
Trimethyldihydroquinoline, 614.
Trimethyldihydroxyethylammonium salts, 807.
Trimethylene chlorobromide, action of aromatic amines and amides on, 1491.
Trimethylene, constitution of, 1163.
—— iodide, preparation of, 1062.
Trimethylenedicarboxylic acids, melting points of, 1040.
Trimethylenedisulphonesulphide, 592.
—— di-, and hexabromo-, 593.
Trimethylenepolycarboxylic acids, thermochemistry of, 1041.
Trimethylenetetracarboxylic acid [1, 1, 2, 2], 1040.
Trimethylenetrisulphone, 591.
—— hexabromo- and tetrachloro-, 592.
Trimethylethylidenelactic acid, β-, 38.
Trimethylfurfurylammonium iodide, 43.
Trimethylgallic acid, nitration of, 716.
Trimethylisopropylammonium iodide, 1295.
Trimethylpropylammonium iodide, 1294.
Trimethylsulphine iodide, 300.
—— preparation of, 1422.
Trimethylthiohydantoïn, 151.
Trimethyl-μ-thiomethylimidazole, $\nu\beta$-, 153.
Trimethylvinylammonium salts, 806.
Triphenyl orthothioacetate, 612.
Triphenylbenzene, symmetrical synthesis of, 993.
Triphenylcarbamide, thio-, 164.
Triphenylethophenazonium hydroxide, amido-, 1109.
Triphenylguanidine picrate, 950.
Triphenyl-γ-hydroxypropylideneacetethylamide, $\alpha\beta\delta$-, 485.
Triphenyl-γ-hydroxypropylideneacetic acid, $\alpha\beta\delta$-, 484.
Triphenylisotriazone, 1471.
Triphenylmethane and chloroform, condensation of, 722.
—— preparation of, 719.
Triphenylmethane-group, dyes of the, 187.
Triphenyl-β-naphthylcarbamide, 167.
—— thio-, 165.
Triphenylpyrrolone, 1003.
Triphenylsulphonebromomethane, 611.
Triphenylsulphonechloromethane, 611.
Triphenylsulphonemethylmethane, 612.
Triphenyltetrahydropyrazine, 634.
Triplite from South Dakota, 1406.
Trisodium imidosulphonate, TRANS., 958.
Trisulphones, 153.
—— formation of, from disulphones, 613, 850.
Trithionate, formation of, by the action of iodine on a mixture of sulphite and thiosulphate, PROC., **1892**, 91.
Tritolylcarbamide, para-, 1083.
Tropeïnes, ψ-, 891.
Tropine, 358.
—— action of hypochlorous acid on, 1014.

Tropine, constitution of, 1244.
Tropine, ψ-, 891.
—— atropate, 892.
Tropyl-ψ-tropeïne, 891.
Truffles of Europe, relation between the terfâs or kamés of Africa and Western Asia and the, 654.
Tscheffkinite, analysis of, 23.
Tubes, block support for, 9.
Tungsten dioxide, action of nitric oxide on, 1152.
—— electrolytic separation of gold from, 920.
—— estimation of, in rich alloys and in steel, 539.
Tungstic acid, action of hydrogen peroxide, on, 944.
—— —— estimation of, 241.
Turkey-red oil, 819.
Turnips, cooked, composition of, TRANS., 227.
Turpentine, action of benzoic acid on, 199.
—— behaviour of, in mixtures of two solvents, 1137.
—— constitution of, 864.
—— detection of, in essences, 386.
—— reaction of, with manganous salts, 386.

U.

Ullmannite from Siegen, 124.
Unsaturated aromatic compounds, action of nitrous acid on, 1198.
Uramidotolyloxamethane, 603.
Uramidotolyloxamic acid, 602.
Uramidotolyloxamide, 603.
Uraninite, new analyses of, 283.
Uranium oxide, action of nitric oxide on, 1152.
Uranous and thorium sulphates, isomorphous, 571.
Urea, cryoscopy of dilute solutions of, 1045.
—— excretion of, 365.
—— mechanism of the production of, in the animal organism, 89.
—— oxalate, 1421.
Urea. See also Carbamide.
Urethanotolyloxamethane, 601.
Urethanotolyloxamic acid, 602.
Urethanotolyloxamide, 601.
Uric acid, estimation of, 546, 1032, 1133.
—— —— excretion of, 365.
—— —— formation of, from cyanacetic acid and carbamide, 149.
—— —— formation of, from nucleïn, 646.
—— —— formation of, in the blood of mammals, 1257.
Uric acid, influence of hot baths on the excretion of, from the human system, 1503.
Uric acid-group, azines of, 70.
Urine, carbonic anhydride in, 649.
—— detection of albumin in, 667, 928.
—— detection of hæmatoporphyrin in, 1136.
—— detection of quinine and phenacetin in, 665.
—— estimation of creatinine in, 1135.
—— estimation of gallic acid in, 924.
—— estimation of homogentisic acid in, 925.
—— ethereal hydrogen sulphates in, 226.
—— excretion of nitrogen in, 1503.
—— hæmatoporphyrin in, 649.
—— human, estimation of phenols in, 544.
—— —— normal, reducing agents in, 1504.
—— —— putrefying, carbohydrates of, 226.
—— in a case of phosphorus poisoning, 650.
—— of animals, occurrence of acetyl derivatives in, after the ingestion of aldehydes, 1504.
—— of hydrophobic rabbits, catechol in, 1115.
—— phosphoric acid in, 1115.
—— sulphates and ethereal hydrogen sulphates in, during diarrhœa, 1505.
—— volumetric estimation of peptones in, 1264.
—— volumetric estimation of sulphuric acid in, 1377.
—— xanthocreatinine in the, 364.
Urohæmatoporphyrin, 744.
Uvic acid, preparation of, 814.

V.

Vacuum, transportation of solids in, by the vapours of metals, 1386.
Valeraldehyde, δ-amido-, 1484.
Valeraldehydeaniline, 1193.
Valeric acid, dibromo-, decomposition of, 960.
Valerolactone, bromo-, 960.
—— hydrolysis of, 1303.
Vanadic acid, action of hydrogen peroxide on, 944.
Vanillenylamidoxime, 318.
Vanillonitrile, 318.
Vanilloylcarboxylic acid, 64.
Vaporisation, heat of, of a solution, 1382.
Vapour densities, determination of, under reduced pressure, 553.
—— density, determinations of, 934.

Vapour pressure, apparatus for the indirect determination of, 679.
—— —— of aqueous solutions of cobalt chloride, 263.
—— —— of water, 396.
—— pressures of solutions, measurement of, TRANS., 769.
Vapour tension of homologous compounds, 396.
Vapours, saturated, of various liquids under the same pressure, temperatures of, 1143.
—— —— pressure and specific volume of, 263.
Vegetable amyloïd, 803.
Vegetable marrow, cooked, composition of, TRANS., 227.
Vegetables, cooked, composition of, TRANS., 226.
—— estimation of pentoses in, 247.
Vegetation, fixation of free nitrogen during, 1508.
—— influence of the nature of the soil on, 1121.
—— of the vine, 908.
—— rain as a source of nitrogen for, 233.
Velocities, relative, of the action of iodine on a mixture of sulphite and thiosulphate, TRANS., 1086.
Velocity of decomposition of diazo-compounds by water, 768.
—— of reaction between alcoholic potash and alkyl halides, 399.
—— —— in mixtures of isohydric and non-isohydric solutions of acids, 936.
Veratroïl, dinitro-, 180.
Vermiculites, constitution of, 125.
Vesuvian from Norway, 1408.
Vicia, analyses of, 522.
Vine, origin of the colouring matter of, 1242.
—— vegetation of, 908.
Vinegar, examination of, 251.
Vinyltrimethylammonium salts, bromo-, 807.
Viscosity of aqueous salt solutions, 1044.
—— of liquids, 1143.
Vitoglycol, 746.
Vitole, 746.
Vivianite from Tamanj, 690.
Volume, E.M.F., and temperature, changes of, on mixing electrolytes, 930.
—— lag, and its bearing on molecular constitution, 1043.
Volumes, Gay Lussac's law of, 1271.
—— molecular, of dissolved substances, 1383.
—— of liquid and gaseous mixtures, 935.
Volumes. See also Specific volumes, Molecular volumes.
Volumeter, gas-, PROC., **1891**, 171.

W.

Water of the lakes of Aiguebelette, Paladru, Nantua, and Sylans, 1061.
Water, composition of, 1271.
—— estimation of dissolved substances in, 920.
—— estimation of fixed and volatile organic matter in, 921.
—— estimation of nitrates in, 243.
—— estimation of oxygen dissolved in, 98; TRANS., 310.
—— expansion of, by heat, 7, 106, 1382.
—— extraction of the dissolved gases in, 1526.
—— from the Arctic Ocean, 1287.
—— influence of, on nitrogenous excretion, 904.
—— influence of temperature on Griess' reaction for nitrites in, 657.
—— maximum density of, 7.
—— mineral, at Sclafani, 25.
—— —— of Monte di Malo, 1287.
—— of crystallisation, 581.
—— rain, ammonia in, 381, 909.
—— refractive power of, at different temperatures, TRANS., 293.
—— solubility of gases in, 107.
—— vapour, saturated, pressure of, 396.
Water-gas, action of, on iron, PROC., **1891**, 126.
Water-generator gas, reconversion of heat into chemical energy by production of, 673.
Waters, mineral, alteration of chalybeate, 1288, 1289.
—— —— aluminium in, 1287.
—— —— at Eilsen, 796.
—— —— preservation of, 1162.
—— natural, colour standard for, 1527.
—— of the North Sea on the coasts of Holland, 419.
—— subterranean, near Port-Vendres, 285.
Wax, detection of resin in, 923.
—— Japan, sp. gr. of, 428.
—— vegetable, assay of bees'-wax for, 551.
—— white, analysis of, 665.
Weighing, rapid, modified balance for, 270.
Weight, live-, influence of various salts on, 647.
Wheat, growth of, in a sterile siliceous soil, 909.
—— proteïds and carbohydrates in, 1119.
Willemite from New Jersey, 1411.
Wine, estimation of glycerol in, 1529.
—— estimation of glycerol, astringent acids, and colouring matter in, 246.

Wine, estimation of potato-starch sugar in, 922.
—— influence of, on peptic digestion, 87.
—— plastered, behaviour of strontium tartrate with, 93.
—— presence of boric acid in, 93.
Wine-lees, estimation of cream of tartar in, 1033.
Wines, decolorisation of, 543.
—— detection of alum in, 1523.
—— sweet, estimation of glycerol in, 1263.
—— —— estimation of tartar in, 1531.
Wolfsbergite from the Harz, 124.
Wollastonite from Perheniemi, Finland, 1407.
Wood, ketones obtained in the dry distillation of, 424.
—— sulphite liquor, 802.
Woollen tissue, detection of vegetable fibre in, 667.

X.

Xanthine, presence of, in the horse's liver, 516.
—— reaction of, 1534.
Xanthocreatinine in the urine, 361.
Xanthones of the naphthalene and quinoline series, 1098.
Xylaldiphenylmaleïde, para-, 482.
Xylalphthalide, para-, 473.
—— —— nitro-derivatives of, 474.
Xylalphthalimidine, para-, 474.
Xylene, meta-, bromonitro-, 1437.
—— —— chloronitro-, 1437.
—— —— cyanonitro-, 1437.
—— —— derivatives of, 1437.
—— —— fluoro-, 968.
—— —— fluoronitro-, 1437.
—— —— iodonitro-, 1437.
Xylenediazopiperidide, nitrometa-, 1437.
Xylenedisulphonic acid, meta-, 1340.
Xylenedisulphonic acid, ortho-, 1341.
Xylenedisulphonic acids, 1340.
Xylenes, action of aluminium chloride on, 1309.
—— separation of the, 1134.
Xylenesulphonic acids, meta-, Proc., 1891, 189.
Xylidine, meta-, action of benzyl chloride on, 314.
—— —— unsymmetrical, action of benzyl chloride on, 1320.
Xylidine, ortho-, chlor-, 1202.
Xylidine zinc chloride, 1455.
Xylitol, 28.
—— constitution of, 29.
Xylitol pentanitrate, 29.
Xylose, 28.
—— constitution of, 29.
—— disappearance of the multirotation of, in ammoniacal solution, 1419.
—— gum in plants which on saccharification yield, 380. 1371.
—— optical properties of, 1420
—— physiological action of, 1506.
—— reactions of, 290.
—— thermochemistry of, 763.
Xylyl methyl ketone, bromopara-, 338.
—— —— —— 3-chloro-1 : 2-, 1202.
—— —— —— parachlorometa-, 1 : 2-, 1201.
—— orthotolyl ketone, 491.
Xylylic acid, nitrometa-, 1437.
Xylylfurfurylcarbamide, meta-, 43.
Xylylfurfurylthiocarbamide, meta-, 43.
Xylylimidazole, *ν*-meta-, 1330.
Xylylimidazolyl-*μ*-mercaptan, *ν*-meta-, 1329.
Xylylimidazolyl-*μ*-methyl sulphide, *ν*-meta-, 1330.
Xylylmethylthiohydantoïn [1 : 3 : 4-], 150.
Xylylphenylketoximes, 490, 491.
Xylylphenylpropionic acid, 849.
Xylylphthalimidine, para-, 474.

Y.

Yeast, hydrolytic functions of, Trans., 593, 926.
—— velocity of the hydrolytic action of, Trans., 928.
—— purification of, 905.
Yeast-cells, effects of varying environment on, Trans., 369.
Yolk of eggs, estimation of fat in, 1134.
Yttrium earth, 1400.

Z.

Zeïn, 749.
Zinc, action of chlorine and of bromine on, 118.
—— action of nitric acid on, 1279.
—— action of, on chromic fluoride, 20.
—— ammonionitrosonaphtholsulphonate, 346.
—— and manganese, separation of, 385.
—— bromide, boiling point of, 680.
—— chloride, boiling point of, 680.
—— cyanide, formation of, from zinc dust, 1164.
—— estimation of, 1129.
—— estimation of, by the ferrocyanide process, 915.
—— fluorovanadite, 788.

Zinc, fluoroxyhypovanadate, 787.
—— fluoroxyvanadate, 787.
—— hydrosulphide, TRANS., 130.
—— lead, and silver, separation of, in galena and blende, 1378.
—— lowering of the freezing point of bismuth by, TRANS., 893.
—— lowering of the freezing point of cadmium by, TRANS., 899.
—— lowering of the freezing point of lead by, TRANS., 905.
—— mercuric cyanide, TRANS., 666.
—— —— thiocyanate, 10.
Zinc nitrates, basic, 1156.
—— orthoborate, 404.
—— oxide, action of hydrogen peroxide on, 1278.
—— separation of manganese from, 537.
—— sulphate, crystallised anhydrous, 941.
—— volumetric estimation of, 534.
Zirconium chloride, preparation of, from zircons, 412.
Zoïsite from Orenburg, 690.

ERRATA.

Vol. LX (Abstr., 1891).

Page	Line	
539	10*	*for* "0·1972" *read* "0·8972."

Vol. LXII (Abstr., 1892).

98	12*	*for*	"T. König" *read* "J. König."
127	6	,,	"dimethylene" *read* "dimethylethylene."
192	17	,,	"dehydroterephthalic" *read* "dihydroterephthalic."
207	7*	,,	"nicotenylazoximepropenyl-ω-carbonic acid" *read* "nicotenyl-azoximepropenyl-ω-carboxylic acid."
248	2	,,	"G. Wiechmann" *read* "F. G. Wiechmann."
297	3*	,,	"*Annalen*, **226**" *read* "*Annalen*, **266**."
359	14	,,	"tro ic acid" *read* "tropinic acid."
,,	23		
364	16*	,,	"Colosanti" *read* "Colasanti."
369	19	,,	"leguminous" *read* "non-leguminous."
394	18	,,	"*Chem. News*, **69**" *read* "*Chem. News*, **64**."
405			Table, col. ii. The unit here employed is the amount of heat required to raise 100 grams of water 1°.
493	15	,,	"*Ber.*, **25**" *read* "*Ber.*, **24**."
506	21*		
544	22	,,	"a diacetate" *read* "an acetate."
578	18*	,,	"E. Rouvier" *read* "G. Rouvier."
596	26	,,	"agetic" *read* "acetic."
613	17		See "A Correction," p. 850.
648	13*	,,	"*fluvatilis*" *read* "*fluviatilis*."
667	bottom	,	"Furbino" *read* "Fubino."
715	13	,,	"Götting" *read* "Göttig."
801	4	,,	"T. B. Lindsey" *read* "J. B. Lindsey."
879	10	,,	"3′-bromoquinoline" *read* "3′-bromoquinoline methiodide."
,,	13	,,	"$C_6H_4<^{N-CO}_{CH:CBr}$" *read* "$C_6H_4<^{NMe\cdot CO}_{CH=CBr}$."
953	11	,,	"P. W. Richards" *read* "T. W. Richards."
965	top	,,	"M. E. Mulder" *read* "E. Mulder."
1030	14*	,,	"Rubricus" *read* "Rubricius."
1074	2	,,	"R. Thal" *read* "K. Thal."
1099	top	,,	"$C_{10}H_6<^{CO}_{O-}>HC_{106}$" *read* "$C_{10}H_6<^{CO}_{O-}>C_{10}H_6$."
1117	12*	,,	"of calves" *read* "and valves."
1118	24	,,	"lauric acid *read* "tannin."
1240	7*	,,	"**absinthum**" *read* "**absinthium.**"
1254	29	,,	"Dunstan and Umney" *read* "Dunstan and Ince."
,,	30	,,	"however" *read* "Dunstan and Umney."
1263	15	,,	"*annum*" read "*annuum.*"
,,	17		

* From bottom.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

THE A. E. STALEY MFG. CO.
RESEARCH and TECHNICAL LIBRARY
DECATUR, ILLINOIS

UNIVERSITY OF ILLINOIS-URBANA
3 0112 062445710